

C471 Part 3. Petroleum Refining and Petrochemicals

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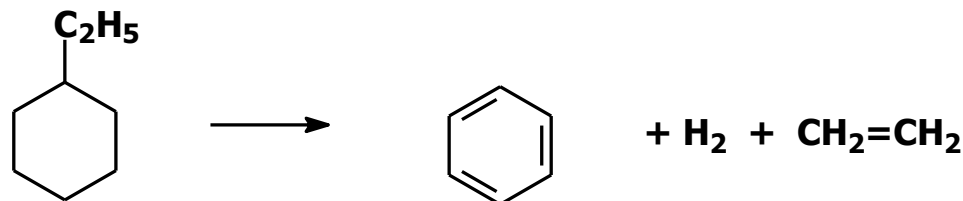
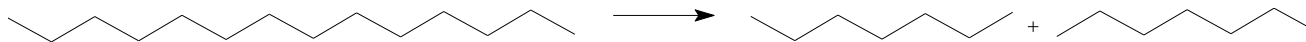
C471 Part 3. Petroleum Refining and Petrochemicals

3.1 Petroleum Refining

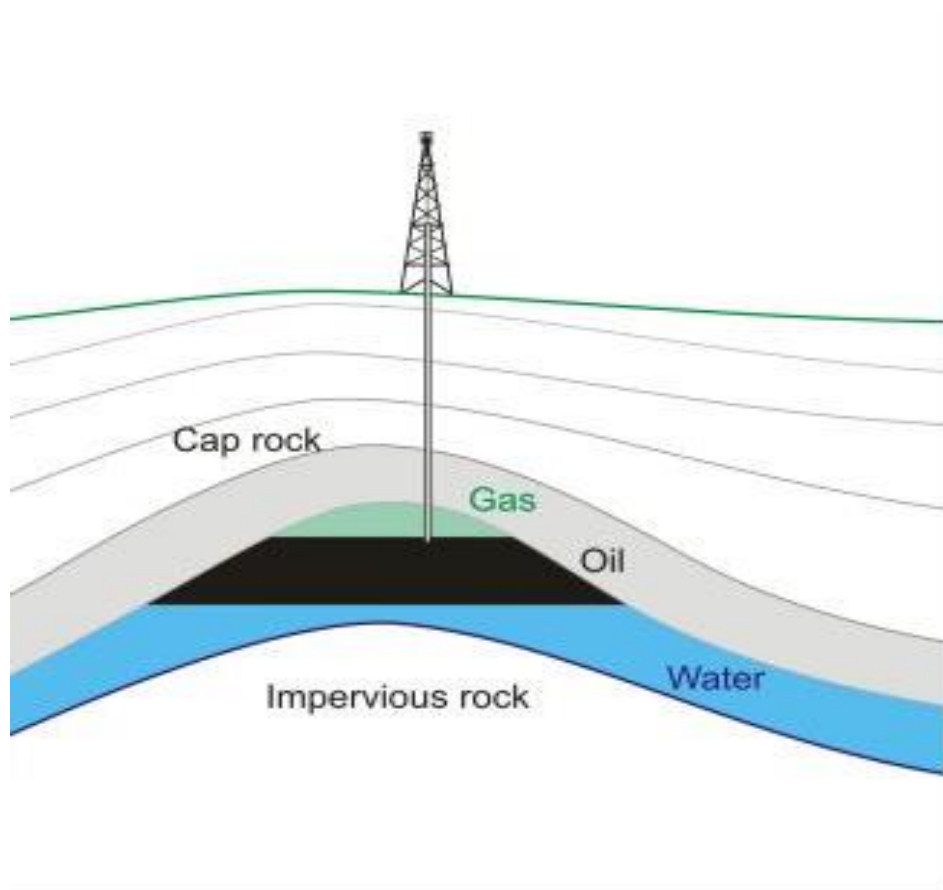
Why refine petroleum?

- to remove impurities (such as water, salt, sulfides)
- use distillation to separate different fractions, such as gasoline (~ C4 to C10)
- use chemical processes to create higher value products (\$\$\$) and adjust the amounts of product to meet market demand (*e.g.*, more gasoline in the summer, more heating oil in the winter)

examples:



Conventional Crude Oil (Petroleum) Well



crude oil: gunk!

Must be refined to make useful products.

Oil Sands

a source of “**unconventional**” crude oil

- **oil sand:** a mixture of sand and clay particles coated with bitumen
- **bitumen:** highly viscous heavy ($> C_{50}$) petroleum resembling tar
- large near-surface deposits found in Alberta, Russia and Venezuela
- bitumen is partially extracted using steam and/or solvents
- requires more refining and upgrading than lighter conventional petroleum



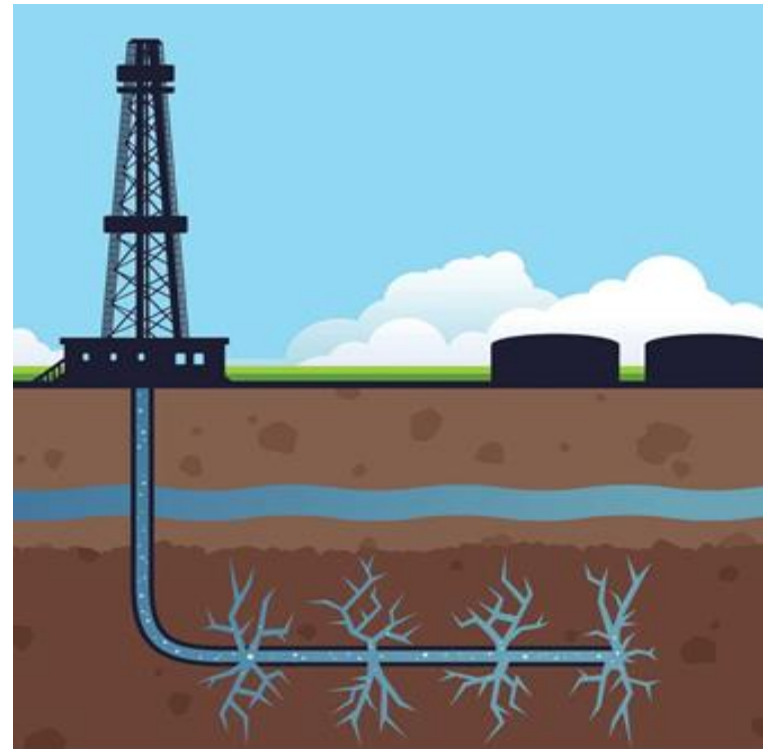
Oil sands mine near Fort McMurray, Alberta

more recently: **Hydraulic Fracturing**

another source of unconventional crude oil

High-pressure fluid (usually water with suspended sand particles and other additives) is used to crack shale and other low-permeability host rock to release **tight** oil and natural gas.

Sand or granular ceramic particles (“**proppant**”) suspended in the fracking fluid keep the fractures in the rock “propped” open.



horizontal drilling into oil-rich rock layers increases well yields

Fracking Fluids

Typically water-based:

90 % water

10 % proppant

1 % chemical additives

Common chemical additives:

Additive

acid (HCl)

thickener (guar gum)

scale inhibitor (ethylene glycol)

corrosion inhibitor (methanol)

biocide (glutaraldehyde)

Purpose

clears debris from bore hole

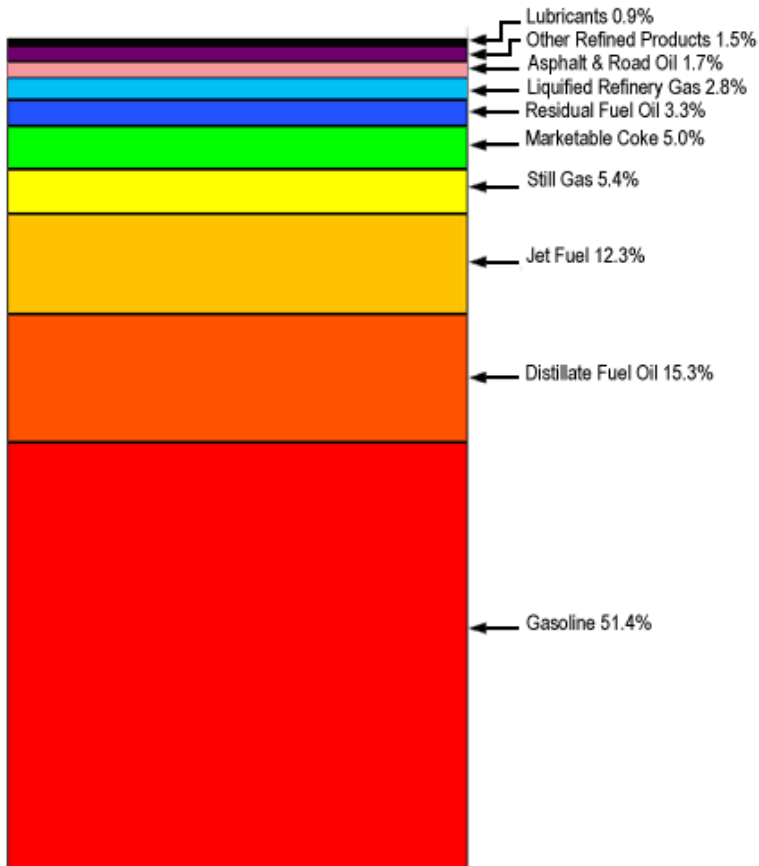
increases viscosity to disperse proppant

prevents carbonate/sulfate deposits

protects steel bore-hole casing

prevents microbial fouling

What's in a barrel of crude oil?



One barrel contains 42 (U.S.) gallons of crude oil. The total volume of products made from one barrel of crude oil is about 48 gallons, 6 gallons larger than the original 42 gallons of crude oil. This "processing gain" is due to the additional other petroleum products (such as alkanes) during refining processes.

1 (U.S.) gallon = 3.7853 liters

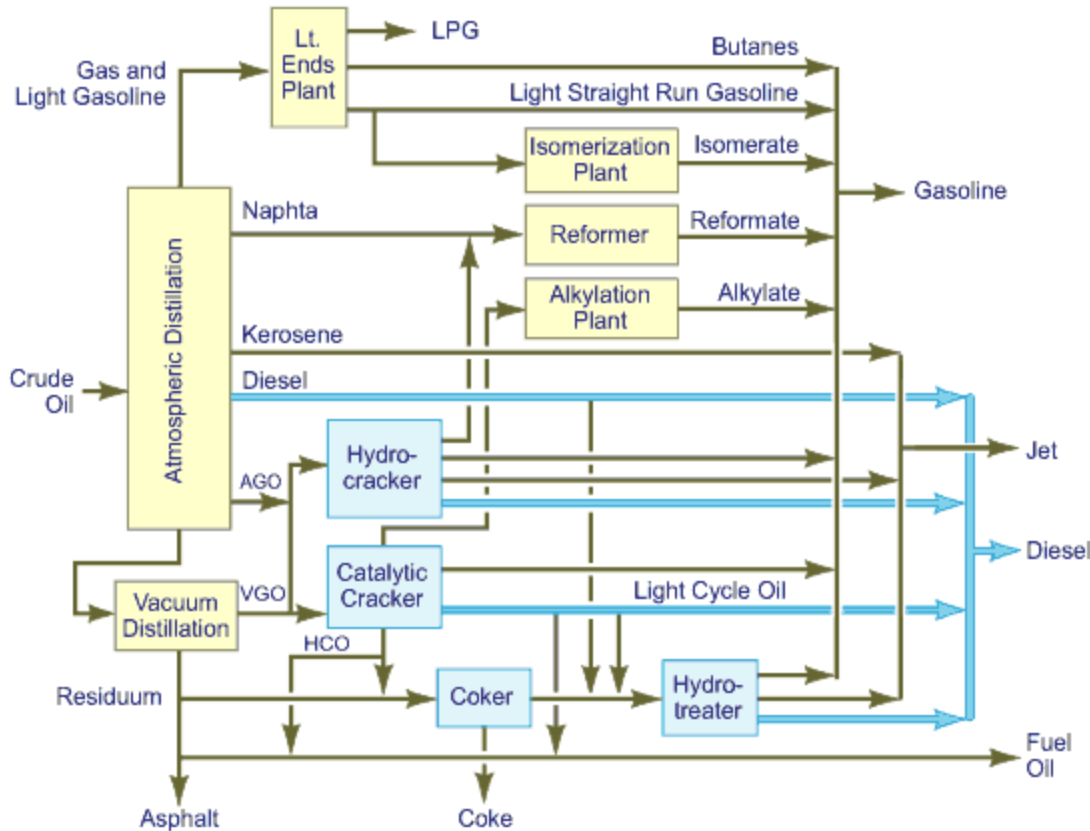
1 (U.S.) barrel = 158.98 liters

Irving Oil Refinery, Saint John NB



What are all those towers, stacks, pipes, tanks, ...?

Schematic Diagram of a Typical Oil Refinery



LPG: liquefied petroleum gas

Reforming: dehydrogenation (aromatization, cyclization, *etc.*)

Hydroprocessing: processes that use hydrogen and a catalyst to remove undesired components

AGO: atmospheric gas oil

VGO: vacuum gas oil

Straight-run products: obtained directly from crude oil distillation with no chemical processing

Petroleum Refining. First Step: Distillation

- thousands of different chemical compounds are present in petroleum
- few are separated as pure substances
- first step in petroleum refining: crude oil is fractionated by distillation
- higher boiling fractions distilled under reduced pressure (“vacuum” distillation)
- each fraction is a complex mixture of chemicals

For example, a gasoline fraction might contain:

- ~ 40 different aliphatic, non-cyclic hydrocarbons
- ~ 30 cycloaliphatic hydrocarbons
- ~ 20 cycloaliphatic hydrocarbons

In addition to water and salts, small amounts of other materials contaminate petroleum:

- carboxylic acids (0.1 to 3 %)
- various sulfides* (allowable level is 0.1 %)
- nitrogen-containing compounds* (only about 0.01 %)

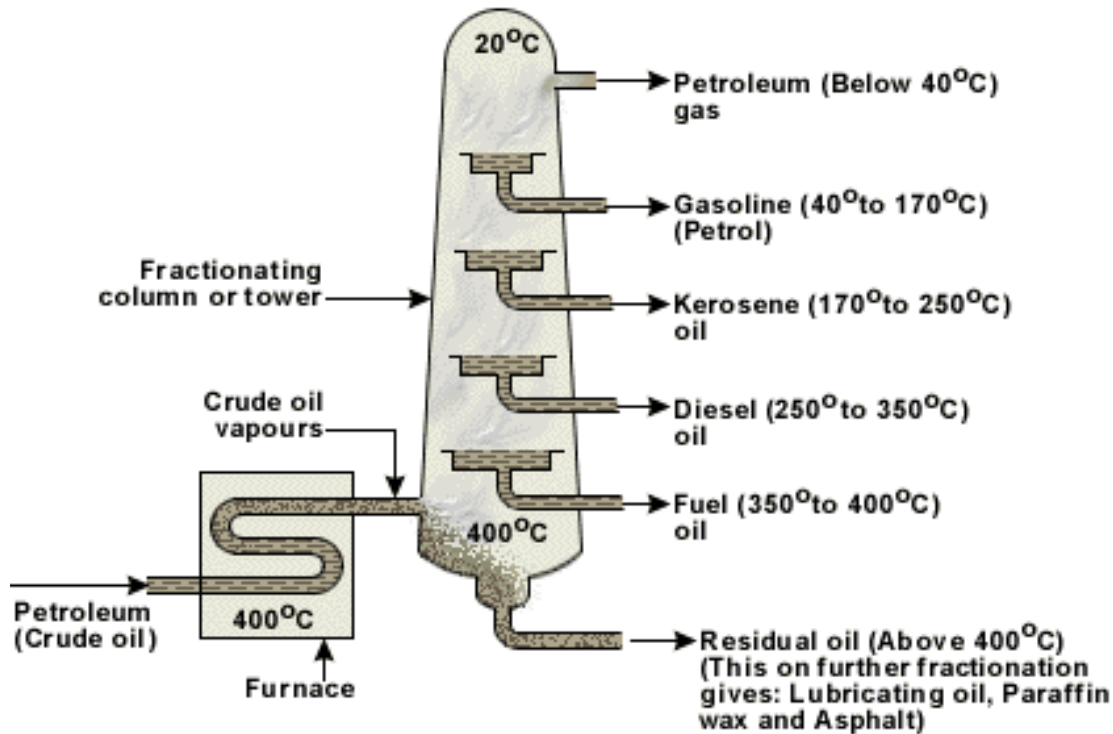
*combustion converts sulfides and nitrogen compounds to SO₂ and NO₂ pollutants

Petroleum Refining: Distillation

approx. b.p. / °C	name	uses
< 20 °C	gases (CH ₄ , C ₂ H ₆ , C ₃ H ₈ , C ₄ H ₁₀)	similar to natural gas, useful for fuel and petrochemicals
20 to 100 °C	light naphtha (gasoline)	C ₄ to C ₆ aliphatic hydrocarbons for gasoline
100 to 150 °C	heavy naphtha	C ₆ to C ₉ aliphatic hydrocarbons
150 to 275 °C	kerosene	C ₉ to C ₁₆ compounds jet, heating, cooking and diesel fuel
200 to 400 °C	gas oil	C ₁₆ to C ₂₅ compounds, diesel and heating fuel
> 350 °C	heavy gas oil	may be cracked to lighter fractions, lubricating and heavy fuel oil
	asphalt	paving, coating, structural uses

Fractional Distillation

(a **physical** refining process)



Fractional distillation of petroleum.

Crude oil enters distillation tower (atmospheric pressure, 20 to 30 m tall) as a foaming stream at about 400 °C.

Heat removed as vapor passes up column, leading to partial condensation and descending liquid reflux streams to improve separation.

The heavy liquid fraction leaving bottom of the main distillation unit is sent to the vacuum distillation column.

Cracking and Reforming

(chemical refining processes)

- petroleum refineries are used to make products in amounts that match current market demand
- more heating oil in winter, more gasoline in summer
- this requires converting fractions for which there is lower demand into more desirable (and more *profitable*) products
- refinery products are used mainly as fuels, but also as petrochemical feedstocks for making industrial organic chemicals
- petrochemicals consume less than 10 % of crude oil production, but command premium prices

product	value
crude oil	1
fuel	2 X
petrochemical feedstock	10 X
consumer product	50 X

One of the main goals of petroleum refining is to produce **high-octane gasoline** for cars and trucks.

Octane Number

- measures the **smoothness with which fuel burns in an engine**
- low octane gasoline gives **knocking** (premature ignition in engine cylinders)
- knocking is bad for engine operation and for gas mileage
- high octane fuel (more expensive) burns more smoothly (better for engines)
- in 1927 a scale was established to define the knocking properties of gasoline
- ***n*-heptane** (the worst test compound) was assigned **octane number 0**
- ***iso*-octane** (2,2,4-trimethylpentane, the best) assigned **octane number 100**
- the **octane number** of a gasoline is defined as the **weight percent isooctane** in an isooctane/heptane mixture that gives the same amount of knocking as the gasoline being tested

Octane Number

There are two octane scales: **research octane number (RON)**
motor octane number (MON)

- RON is determined using a standard ASTM engine of defined characteristics
- MON is determined under road conditions
- $\text{MON} < \text{RON}$ by about 10 points
- the rating on the pumps is $(\text{RON} + \text{MON})/2$
- octane number increases with the amount of branching, rings and multiple bonds
- octane numbers are generally in the order:

alkenes, aromatics, alkynes > cyclic and branched alkanes > *n*-alkanes

- Why?

Octane Number

Representative octane numbers:

Compound	Octane #	Compound	Octane #
<i>n</i> -octane	-19	2,2,4-trimethyl-1-pentene	102
<i>n</i> -heptane	0	benzene	105
<i>n</i> -hexane	25	ethylbenzene	107
2-methylhexane	42	<i>o</i> -xylene	104
<i>n</i> -pentane	62	cumene	113
cyclohexane	83	<i>p</i> -xylene	116
trans-2-hexene	93	<i>m</i> -xylene	118
isooctane	100	toluene	120
cyclopentane	101		

note that some octane numbers < **0** or > **100**

Chemical Reactions Used in Refineries

1) Hydrotreating (also called hydrocracking) (*not “water-treating”!*)

Converts unwanted S, N, O in petroleum into H_2S , NH_3 , H_2O for removal.
Uses hydrogen from the other refinery processes, such as reforming.
Can be used to upgrade heavy feedstocks to higher-value products.

2) Cracking Processes

- a) making smaller molecules from larger ones
- b) converting saturates, such as ethane or propane, into ethylene, propylene and other olefins (\$\$\$)

Two main kinds of refinery cracking processes:

- **thermal (steam) cracking** used for both **a)** and **b)**
- **catalytic cracking** used for **a)** and for making branched chain molecules and aromatics

3) Catalytic Reforming

Dehydrogenates both straight chain and cyclic aliphatics into aromatics over Pt or Re catalysts

Chemical Reactions Used in Refineries

4) Polymerization

Combines low molecular weight olefins into gasoline-range molecules using H_2SO_4 or H_3PO_4 catalysts (*not used much now*)

5) Alkylation

Combines an olefin with a paraffin (*e.g.*, isobutylene with isobutane) to give branched chain molecules. H_2SO_4 and HF are used as catalysts. Important for making high octane gasoline.

6) Isomerization

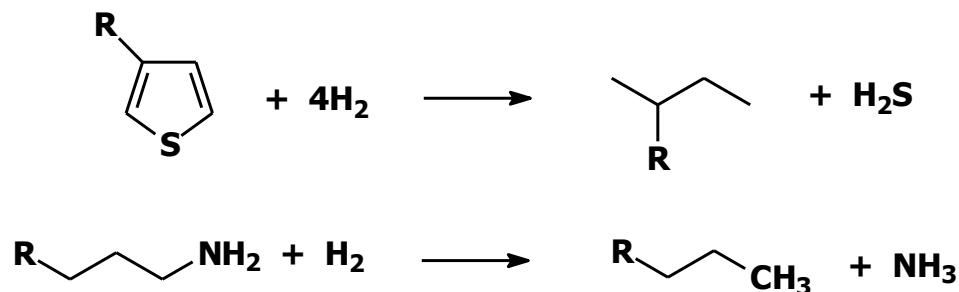
Used to convert straight chain to branched chain compounds. (Butane to isobutane, ethylbenzene to o-xylene, m-xylene to p-xylene). Also very important to get high octane gasoline.

Hydrotreating (aka Hydrocracking)

reduces the sulfur and nitrogen content of petroleum

- distilled petroleum fractions contain sulfur and nitrogen compounds:
 - S as mercaptans (R-SH), thiaalkanes (R₁-S-R₂), disulfides (R₁-S-S-R₂), thiophenes
 - N as amines and heterocyclic compounds
- sulfur and nitrogen compounds in fuels are environmental pollutants
- **sulfur poisons catalysts** used in the chemical processing of petroleum
- before these processes occur, hydrotreating is used to reduce S, N levels
- petroleum fractions are reacted with hydrogen

**typical
hydrocracking
reactions**



- the H₂S and NH₃ produced by hydrotreating are easily removed

Hydrotreating (*aka* Hydrocracking)

- distilled petroleum fractions are reacted with H₂:
 - at 300 to 400 °C for light naphtha
 - at 350 to 425 °C for heavier fractions (less reactive)
- catalysts are cobalt oxide, molybdenum oxide and nickel oxide
- acid gases H₂S and NH₃ produced by hydrotreating reactions are chemically removed using aqueous NaOH scrubbers
- up to 99.5 % nitrogen and 99.95 % sulfur is removed

undesirable hydrotreating side reaction:

- some carbon-carbon double bonds are hydrogenated
- this decreases the octane rating
- further processing (catalytic cracking) can restore the octane rating

Thermal Cracking (aka Steam Cracking)

the only source of olefins for the chemical industry

- ethylene and propylene are the most important feedstocks for petrochemicals
- used directly or indirectly in the synthesis of 60 % of industrial organic chemicals
- **problem** due to their high chemical reactivity, only trace amounts of ethylene, propylene and other olefins are present in petroleum
- **solution** use thermal cracking to synthesize ethylene, propylene, other olefins
- **ingenious and simple technology** **no catalysts, no added chemical reagents,** just partial thermal decomposition of alkanes in steel reactor tubes at about 1000 °C

typical
thermal cracking
reactions

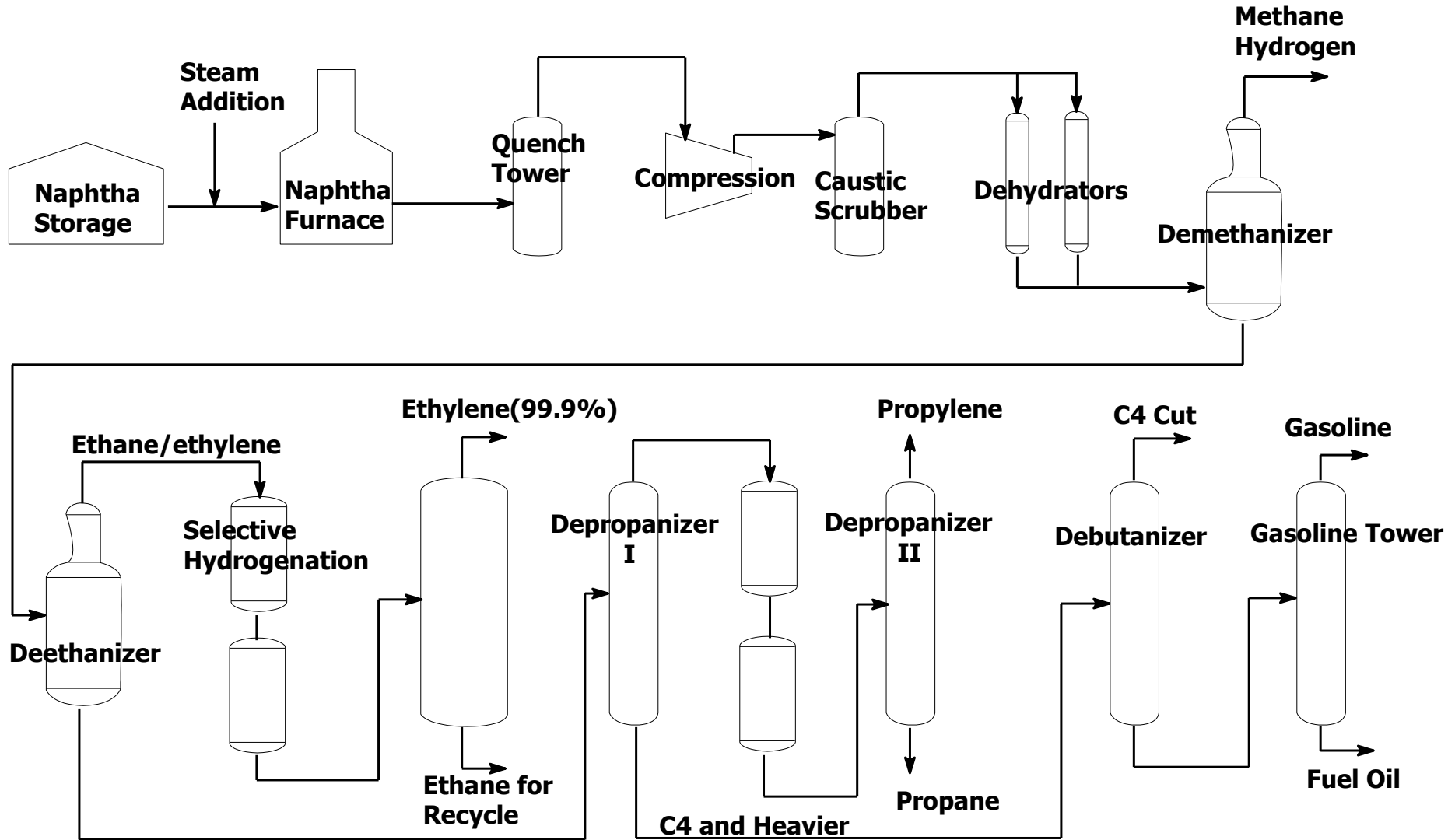


Thermal Cracking (aka Steam Cracking)

- uses higher temperatures (1000 °C) than hydrotreating
- as a result, the reactions are very fast (no catalyst required)
- short reactor residence times (can be *milliseconds*)
- inlet streams can be supersonic
- cracked products exit the reactor tubes at about 850 °C (• Why cooler than inlet?)
- thermal crackers operate at reduced pressures (• Why?)
- steam used as a diluent to reduce reactant partial pressures (• Why?)
- products are rapidly cooled to 300 °C to avoid unwanted secondary reactions such as oligomerization and coking
- **coking** (thermal cracking “gone too far”) reduces olefin yield and leaves a solid carbon deposit on the reactor tubes, *e.g.*: $\text{H}_2\text{C}=\text{CH}_2(\text{g}) \rightarrow 2\text{C}(\text{s}) + 2\text{H}_2(\text{g})$
- steam reduces unwanted coking: $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$

Thermal Cracking Flow Diagram

(a diagram can be worth a thousand words)



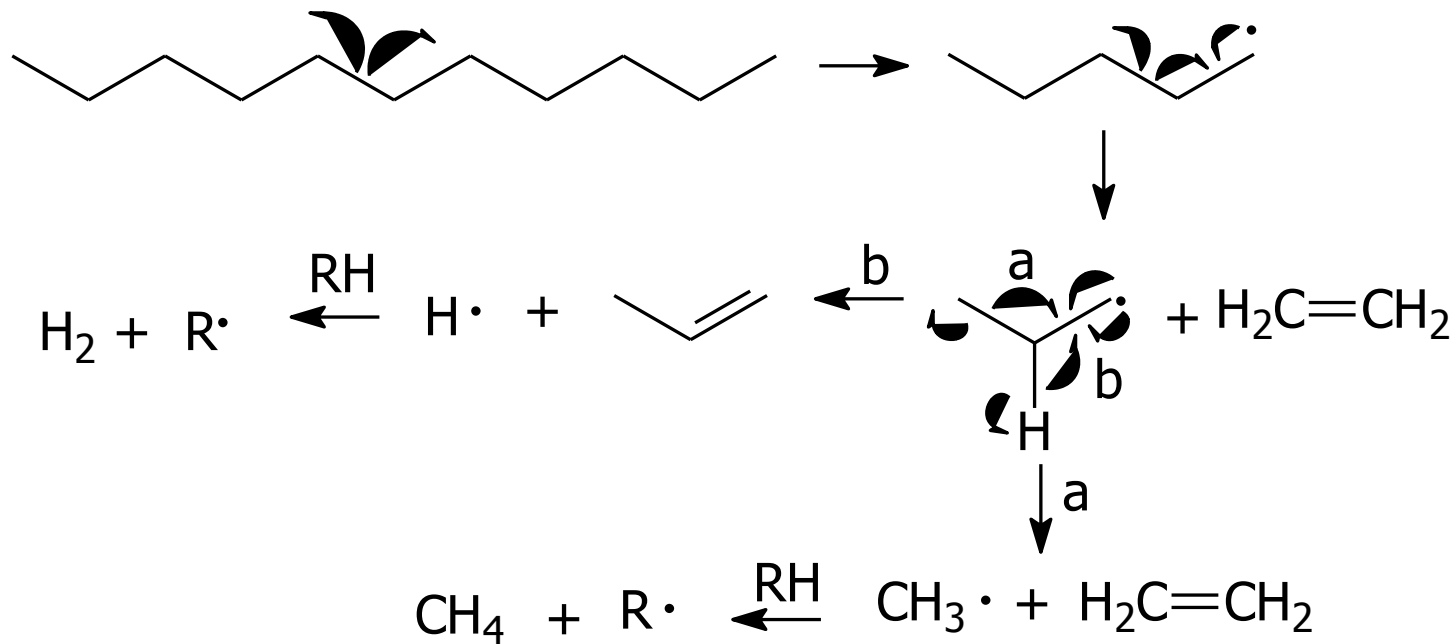
Thermal Cracking Flow Diagram

(a diagram can be worth a thousand words)

- thermal cracking gives higher yields of C₂, C₃, C₄ olefins than higher olefins
- gases leaving thermal crackers contain small amounts of H₂S, CO₂, H₂O from the hydrogenation of sulfur and oxygen impurities in the feed
- the gases are scrubbed to remove CO₂ and H₂S then dried with molecular sieves
- the purified gases are distilled in a **demethanizer** tower with a condenser cooled to -95 °C with liquid ethylene
- methane and hydrogen are the demethanizer top products, C₂+ are the bottoms
- the C₂+ stream from the demethanizer is distilled in a **deethanizer** column
- the C₂ tops from the deethanizer are selectively hydrogenated to remove acetylene then distilled to give ethylene (tops) and ethane (bottoms, for recycle)
- C₃+ bottoms from the deethanizer are distilled in a **depropanizer** column
- C₃ tops from the depropanizer are distilled to separate propane and propylene
- C₄+ bottoms from the depropanizer are distilled in a **debutanizer**
- debutanizer C₄ tops are solvent extracted with acetonitrile to separate butane and butadiene (boiling points too close to be separated by fractional distillation)
- the C₅+ debutanizer bottoms are distilled to separate cracked gasoline fractions from heavier kerosene and fuel oil products

Thermal Cracking Chemistry

- C-C bonds are difficult to activate at room temperature
- not at 1000 °C where
 - ◆ entropy dominates
 - ◆ free radicals are stable
- fascinating free-radical reaction mechanisms
- high- T reactions are not covered in most chemistry programs

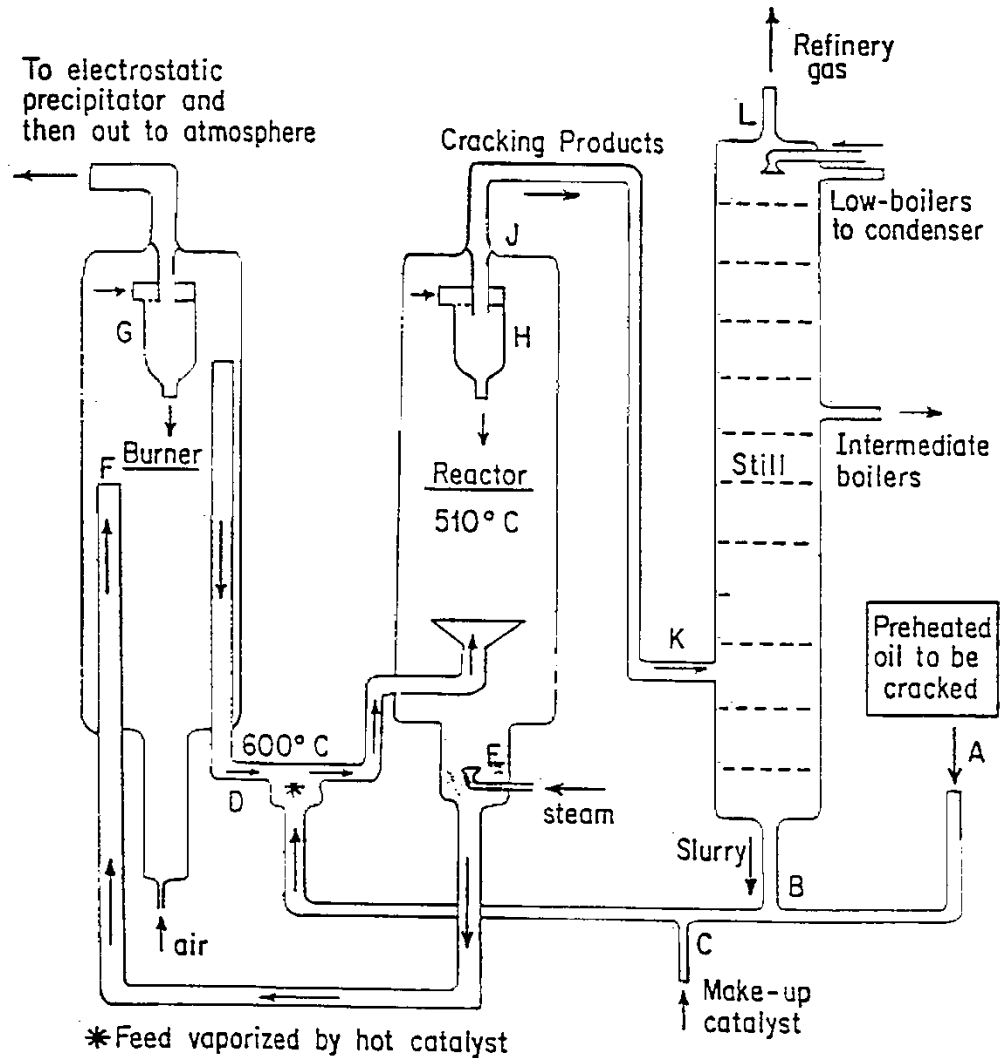


Catalytic Cracking

- used on heavy naphtha and gas oil feedstocks
- products are mainly isoalkanes (good for gasoline), *n*- and iso-olefins and *n*-alkanes from C₃ up
- feedstock is C15 to C25 and the product is mostly C4 to C10
- little ethylene forms, but there is some propylene
- the catalyst is aluminum silicate or an alumina-silica mixture or a **zeolite** (often supported on tougher alumina particles)
- catalyst may be a bed of beads or **fluidized** powder (better)
- in a typical fluidized-bed reactor, several hundred tons of catalyst are in circulation, more than three million gallons of liquids are produced per day
- the reaction temperature is 465 to 540 °C
- pressure between 0.7 and 1.3 bar
- the oil:catalyst ratio is about 4:1

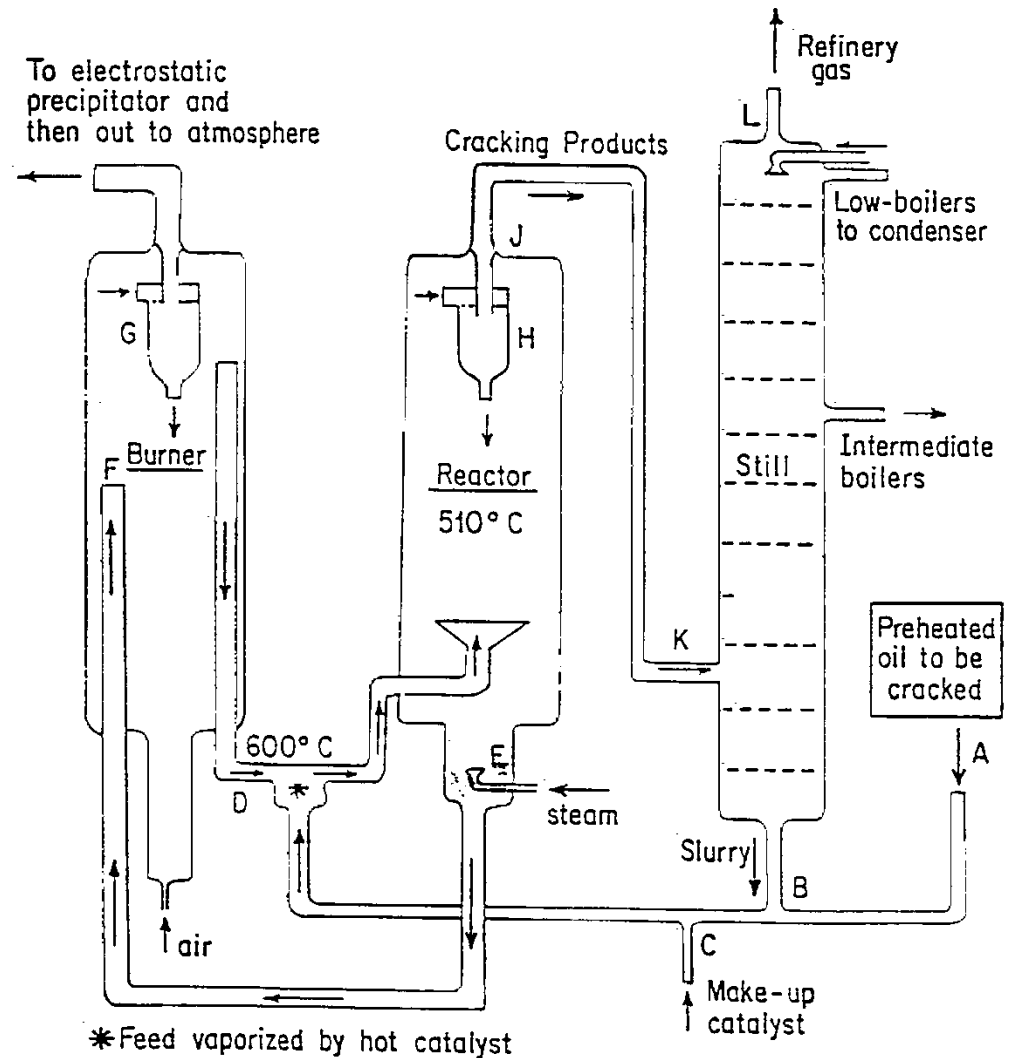
Catalytic Cracking

1. high MW compounds such as gas oil are preheated and enter at **A**
2. new catalyst continuously added at **C**
3. some finely-pulverized catalyst is lost on each cycle, making it past the **cyclone at G)**
4. catalyst particles coated with carbonaceous products fall to the bottom of the reactor
5. steam entering at **E** strips off any volatile material which is carried upward to react further
6. residual carbonaceous coating is burned off in the burner



Catalytic Cracking

- clean hot catalyst particles mix with the feed at **D** (hot catalyst is the main source of heat for the reactor)
- the product stream leaves the reactor at **J**, enters the still at **K**
- the refinery gas (**L**) is mostly H_2 , ethylene, propylene, and butylenes
- low boiling and intermediate fractions are also taken off the still as shown
- at **B**, heavy hydrocarbons which were not sufficiently cracked in the previous pass, join the stream with any catalyst making it past the cyclone separator **H**



Catalytic Cracking

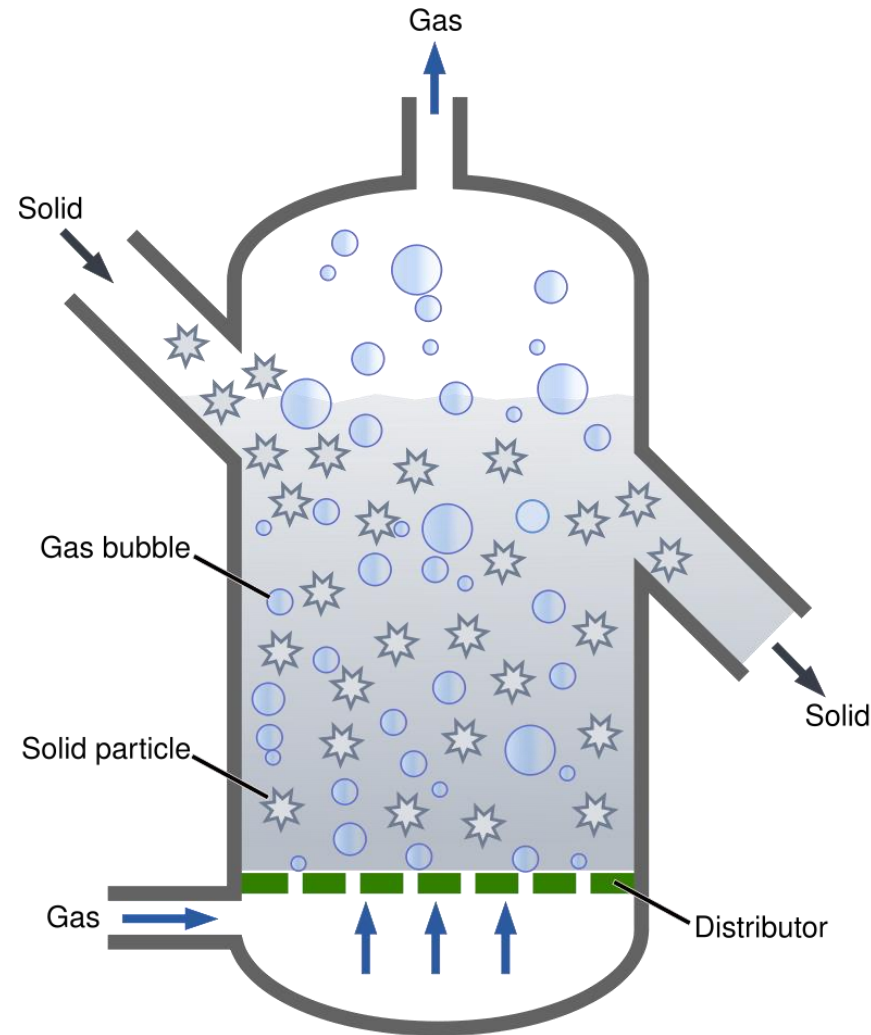
Fluidized Bed Reactor

Instead of pumping the hydrocarbon gas over a bed of fixed catalyst particles, the flowing gas is used to suspend powdered catalyst particles in the flowing stream causing the particles to behave as a fluid.

- uniform mixing
- very high mass transfer rates
- no reactor “hot spots”

but

- higher pumping costs
- larger reactor size
- some erosion of internal reactor parts



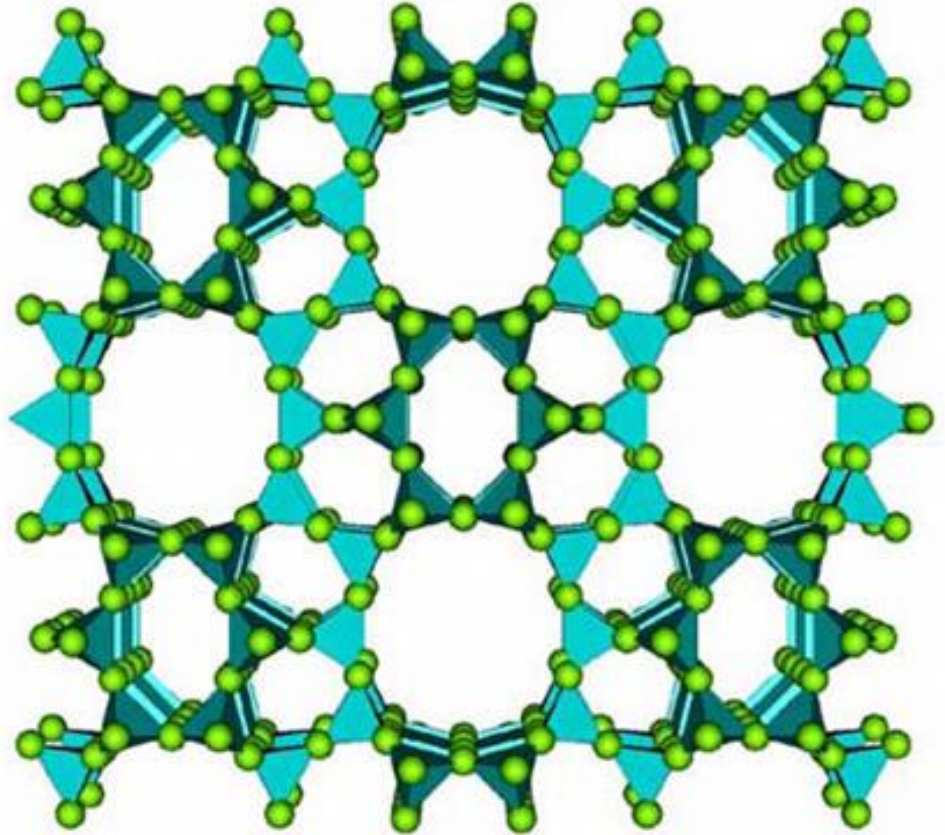
Catalytic Cracking

Zeolites

Microporous (< 2 nm pores) and mesoporous (2 to 50 nm pores) aluminosilicate minerals.

Used as catalysts and as adsorbents.

Zeolites confine reacting molecules in small cages, changing their structure and reactivity.

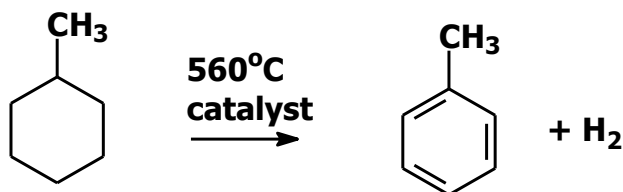


Catalytic Reforming

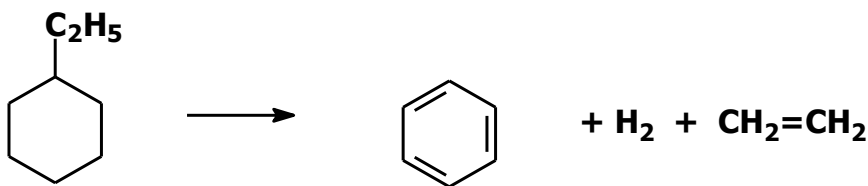
Catalytic reforming leaves the number of carbon atoms in the feedstock molecules unchanged, but increases the number of double bonds and aromatic rings.

typical catalytic reforming reactions:

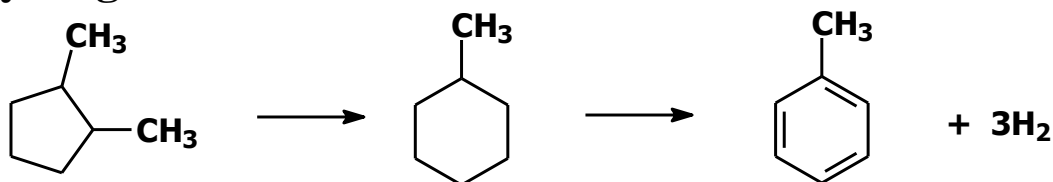
dehydrogenation



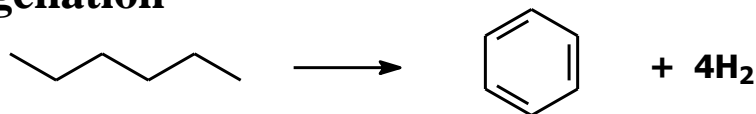
dealkylation and dehydrogenation



rearrangement and dehydrogenation



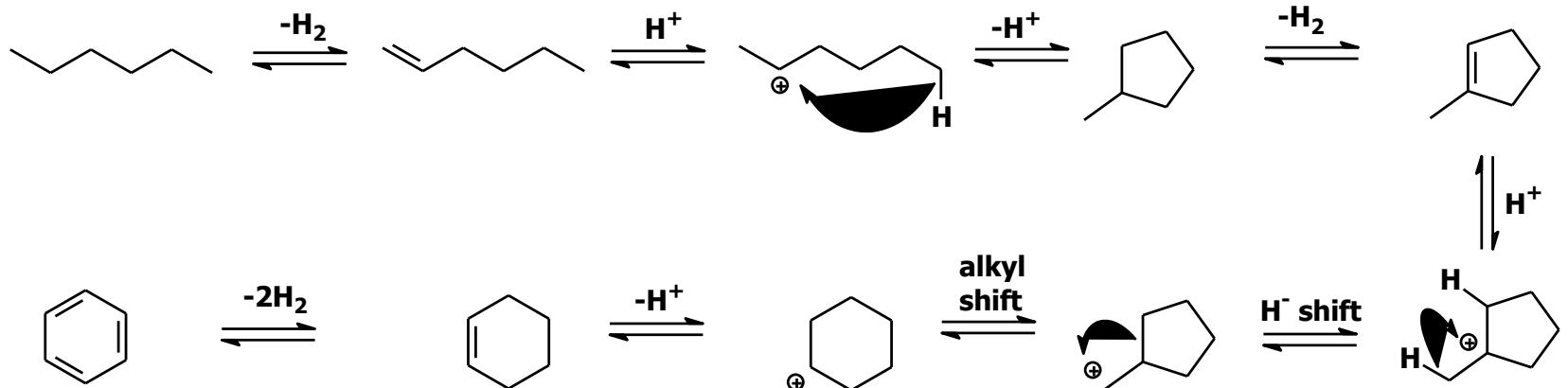
cyclization and dehydrogenation



Catalytic Reforming

- catalytic reforming is the main process for upgrading gasoline
- low-octane straight run gasoline can be reformed to contain 40 to 50% aromatic hydrocarbons, of which 15 to 20% is toluene
- also the main source of **BTX** (**B**enzene-**T**oluene-**X**ylenes) petrochemicals
- high temperatures and platinum/rhenium catalysts on alumina are used
- hydrogen is added to reduce the rate of dehydrogenation

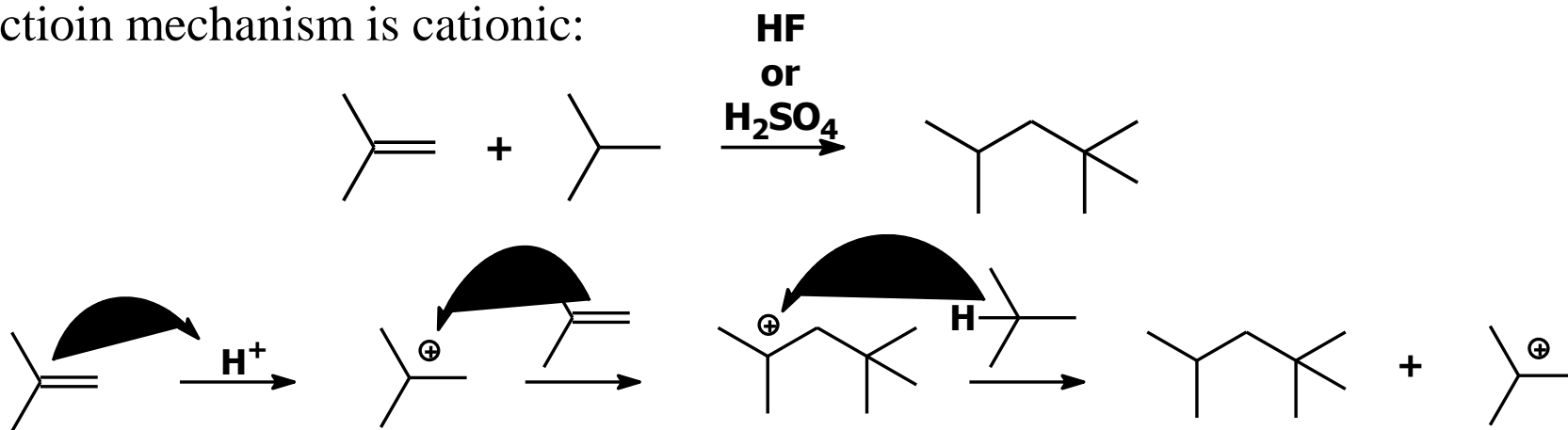
typical catalytic reforming mechanisms:



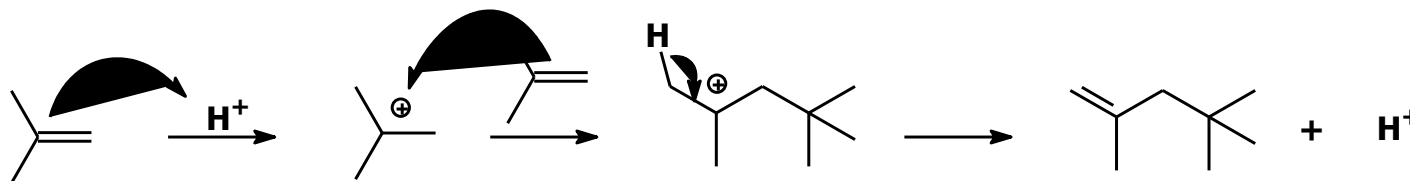
Other Refinery Processes

Cracking and reforming are by far the most important refinery processes, especially for the production of petrochemicals, but a few other processes deserve mention:

1. Alkylation Alkanes react with olefins in the presence of an acid catalyst to give highly branched alkanes. For example, isobutylene and isobutane react to give isooctane to be added to straight run gasoline to boost the octane number. The reaction mechanism is cationic:

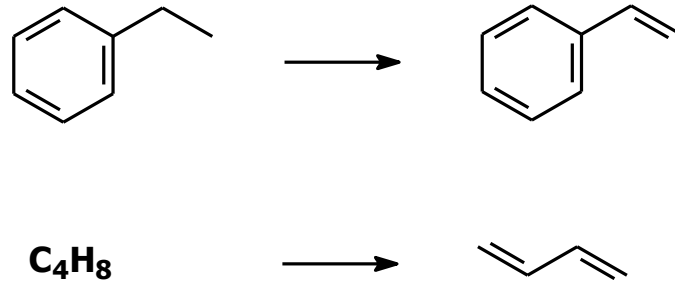


2. Polymerization Olefins react to form dimers, trimers, *etc.*

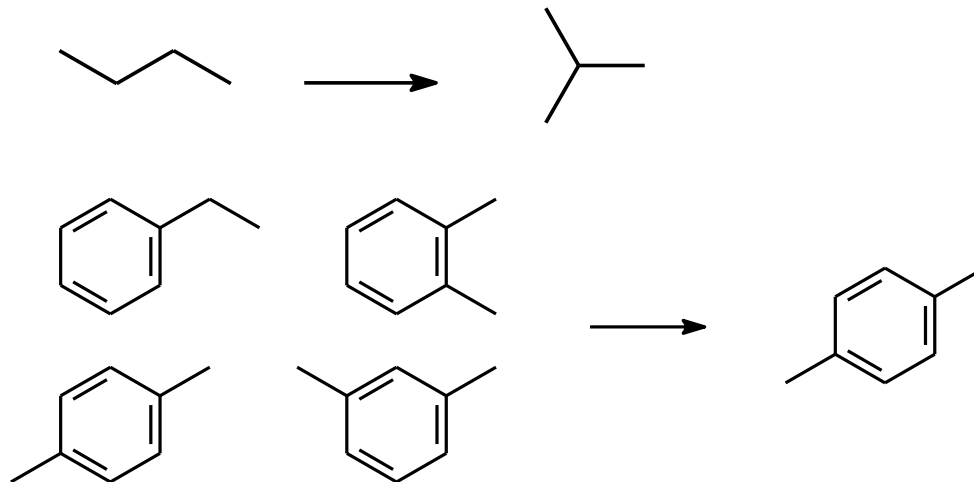


Other Refinery Processes

3. Dehydrogenation For example, the conversion of ethylbenzene to styrene and the conversion of butene to butadiene. Styrene and butadiene are especially valuable for the production of industrial polymers



4. Isomerization Converts straight-chain hydrocarbons to branched molecules.

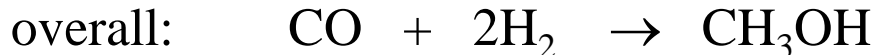


3.2 Chemicals from Methane (C1 Chemistry)

Methanol

- methanol is one of the top ten organic chemicals
- 50 % used to make formaldehyde, which is used to make urea-formaldehyde and formaldehyde-phenol resins

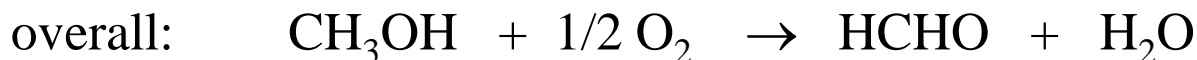
- methanol is synthesized from CO and H₂ in two exothermic steps:



- reactor operated at 300 to 400 °C and 300 bar with CuO/ZnO catalyst on Al₂O₃
(• How is the CO/H₂ feed produced? • Why use high pressure?)
- only ~ 20 % conversion per pass, so recycling reactants is essential
- fascinating chemistry (still not understood):
 - ◆ isotopic labeling indicates CH₃OH is produced by hydrogenation of CO₂ (not CO) formed by the reaction of adsorbed CO with atomic O which is formed by the dissociation of adsorbed H₂O
 - ◆ rate determining step is the hydrogenation of adsorbed H₂COO species

Formaldehyde (C1 Chemistry)

- 50 % of methanol is used to make formaldehyde (HCHO)
- formaldehyde is synthesized by the partial oxidation of methanol in two steps:



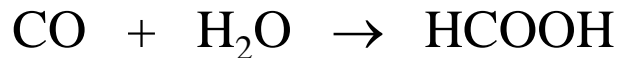
- one process uses red-hot silver catalyst at 600 to 700 °C
- a 2nd process uses more-active Fe₂O₃/MoO₃/Co₂O₃ catalyst at 300 to 400 °C
- hot gases from the reactor are cooled and washed with water to absorb HCHO
- formaldehyde dissolved in water at 37 wt % is shipped
- 1 to 2 % methanol can be added to reduce polymerization

applications:

- aqueous formaldehyde is a disinfectant and preservative (FormalinTM)
- formaldehyde is used to make polyhydric alcohols, such as pentaerythritol
- anhydrous formaldehyde or its trimer (trioxane) is important for making thermoplastics, such as urea-formaldehyde resins

Other C1 Chemistry

formic acid (the simplest carboxylic acid)



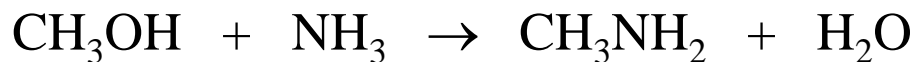
formic acid esters



acetic acid by methanol carbonylation



methylamine



formamide



3.3 Chemicals Derived from Ethylene (C2 Chemistry)

Most ethylene is synthesized by thermal (steam) cracking of hydrocarbons at high temperatures (about 1000 °C), no catalyst required.

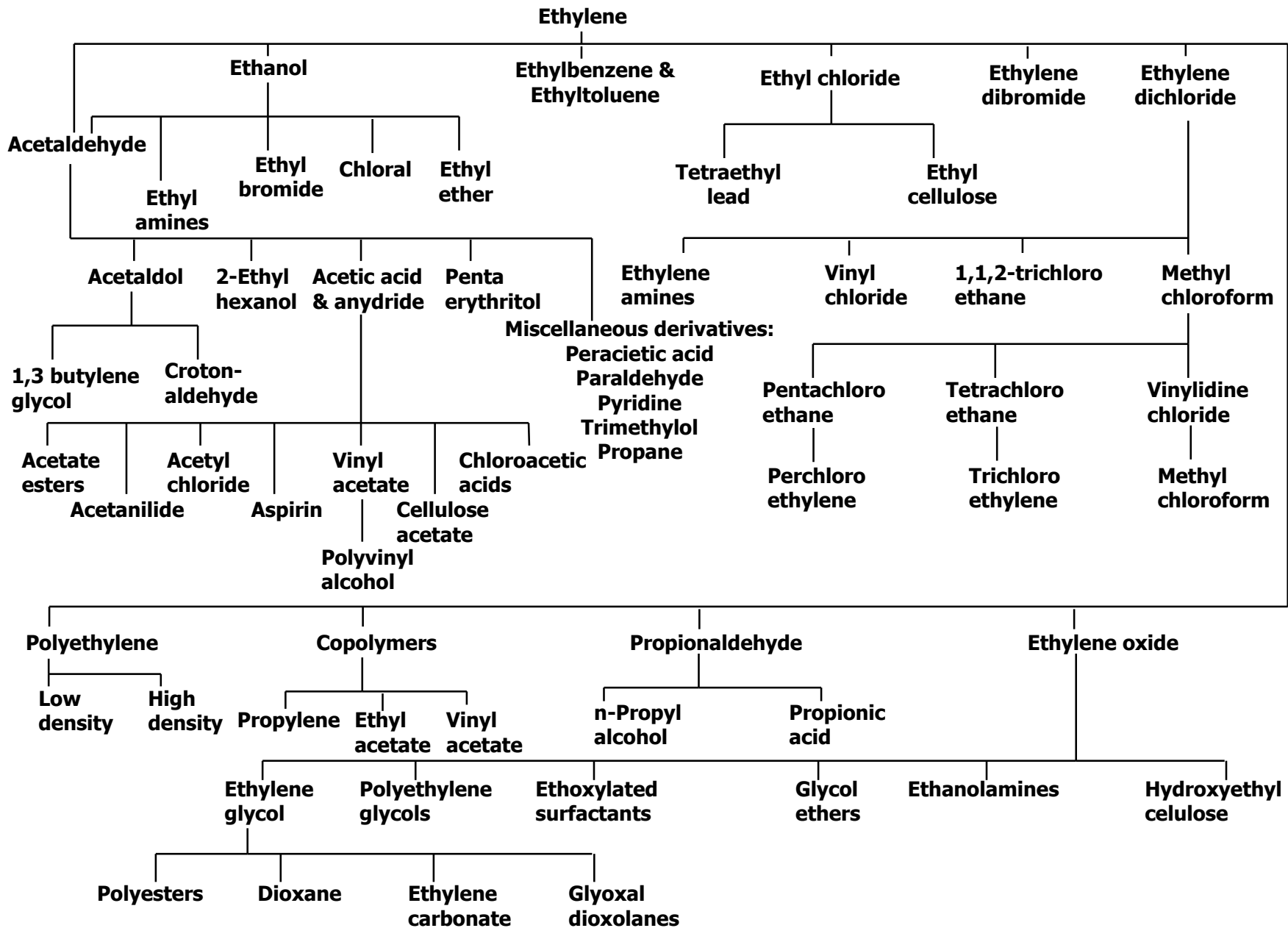
Distilling the C2 stream from thermal crackers gives 95 to 99.9 % pure ethylene.

About 60 % of ethylene production is used to make polyethylene, the most important industrial polymer.

Other major organic chemicals derived from ethylene:

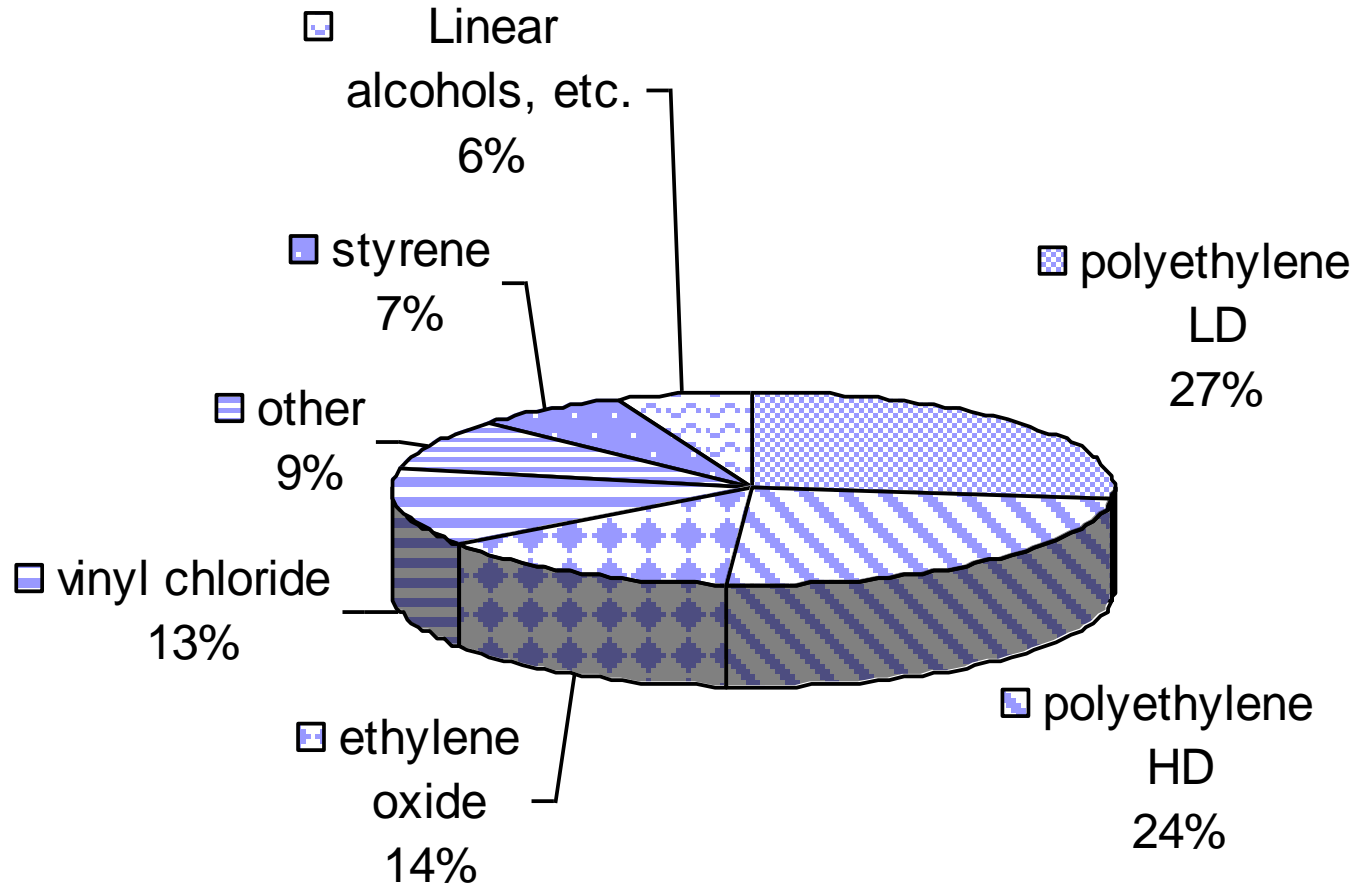
- ethylene oxide for the manufacture of ethylene glycol and polyester fibres
- vinyl chloride for the manufacture of PVC
- styrene for the formation of polystyrene
- linear alcohols and olefins for detergents

Chemicals Derived from Ethylene



Chemicals Derived from Ethylene

Uses of ethylene

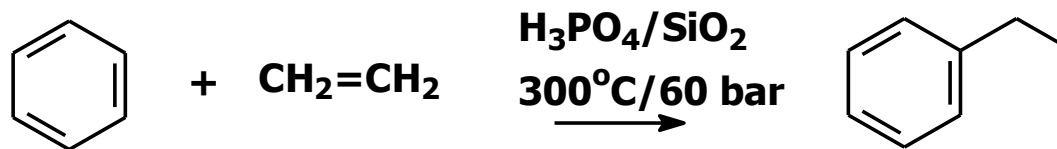


Chemicals Derived from Ethylene

Ethylbenzene from Ethylene and Benzene

Two commercial processes are used:

1. Gas-Phase Ethylation



- ethylene reacts with the acid catalyst to generate a carbocation-like complex
- this system does not transalkylate or dealkylate
- essential to use an excess of benzene to avoid over ethylation

more important:

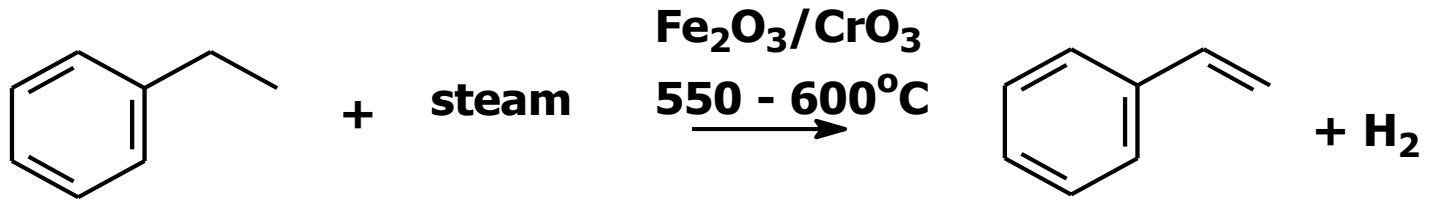
2. Liquid-Phase Friedel-Crafts Ethylation

- carried out at 90 °C in a countercurrent bubble reactor
- Friedel-Crafts catalysts such as AlCl₃, BF₃, H₃PO₄
- excess benzene is used to prevent overalkylation
- a four-column distillation unit is required to purify the ethylbenzene

Chemicals Derived from Ethylene

Styrene from Ethylbenzene

- endothermic dehydrogenation with superheated steam
- the steam is also used to lower the partial pressure of ethylbenzene
- $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3$ catalyst (less active than lab-scale Pt or Pd catalysts, but cheaper)



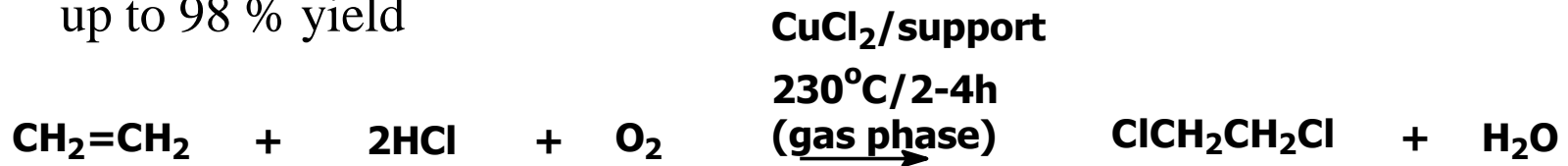
- reaction is run at 550 to 600 °C
- extension of delocalization is a helpful driving force
- ethylbenzene, boiling point 136 °C
- styrene, boiling point 145 °C
- as a result, it takes four distillation columns to get clean product
- additives such as butylated hydroxytoluene (BHT) are essential to prevent styrene polymerization

Chemicals Derived from Ethylene

Ethylene Dichloride (EDC)

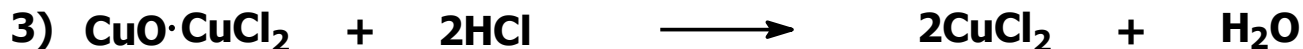
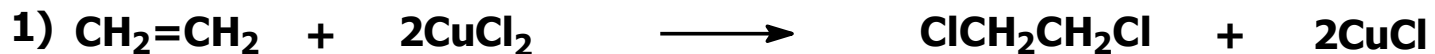
1. Addition of Chlorine to Ethylene (older method)

- bubble-column reactor using the EDC product as the liquid phase solvent
- operated at 40 to 70 °C and 5 bar with dissolved FeCl₃, CuCl₂ or SbCl₃ catalysts
- up to 98 % yield



2. Oxychlorination of Ethylene Using Air and HCl

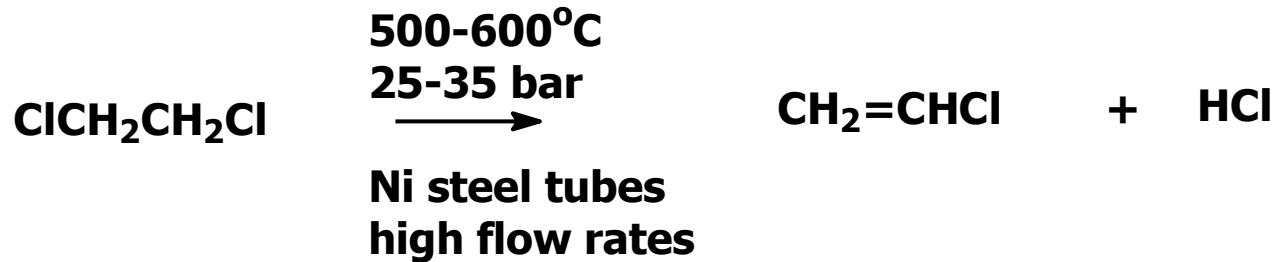
- expensive Cl₂ not required, instead CuCl₂ is used to transfer Cl to ethylene
- CuCl produced is recycled because it is readily oxidized by air
- HCl is oxidized to Cl₂ (2HCl + 2Cu²⁺ → Cl₂ + 2Cu⁺ + 2H⁺) but only as needed



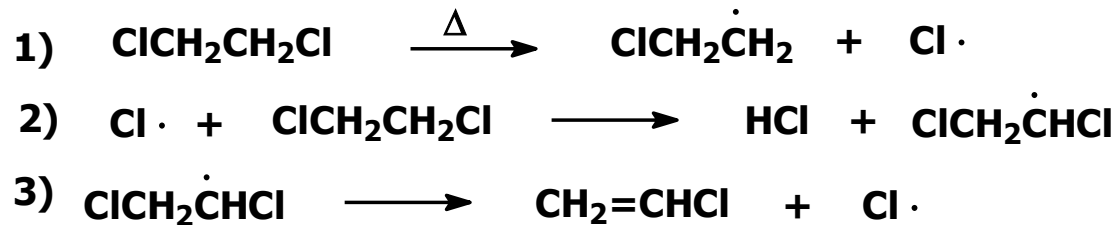
Chemicals Derived from Ethylene

Vinyl Chloride ($\text{H}_2\text{C}=\text{CHCl}$)

- could be prepared by dehydrohalogenation of ethylene using NaOH, but this is too costly on an industrial scale
- instead, a high-temperature gas-phase thermal reaction is used
- no catalyst required
- reactors tubes made of corrosion-resistant stainless steel
- HCl generated by the process is recycled to the chlorination reactor



proposed mechanism

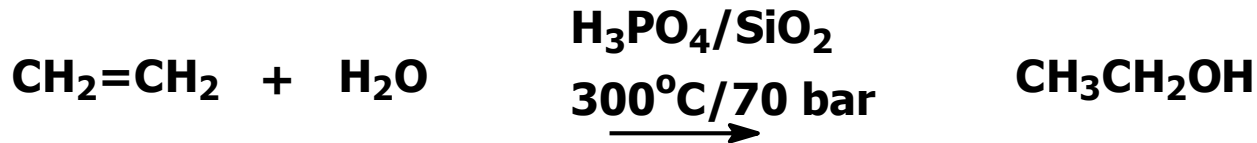


- polymerization of vinyl chloride to PVC uses about 15 % of ethylene production

Chemicals Derived from Ethylene

Hydration to Ethanol

- an older process used the hydration of ethylene with aqueous sulfuric acid
- ethyl sulfate, an intermediate, needed to be hydrolyzed
- **a gas phase reaction is now used**, with a phosphoric acid catalyst
- a low conversion per pass over the catalyst is necessary because too much water would wash the acid catalyst from the support
- the reaction is slow due to the rate-determining generation of a primary carbocation



- gas-phase hydration of ethylene became the cheapest way to make ethanol once ethylene from petroleum refining became a major industrial commodity

Fermentation Ethanol Fermentation as a source of ethanol was restricted to beverage alcohol until recently when interest in ethanol as a motor fuel was motivated by oil shortages. It is not clear whether fermentation ethanol fuel (mostly from corn) is economical considering government subsidies and the costs of crop production, fertilizers, fermentation and distillation.

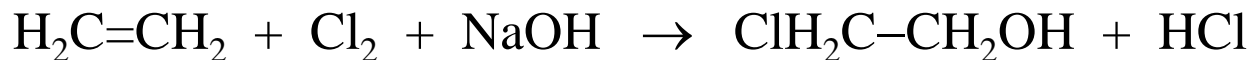
Chemicals Derived from Ethylene

Oxidation of Ethylene to Ethylene Oxide

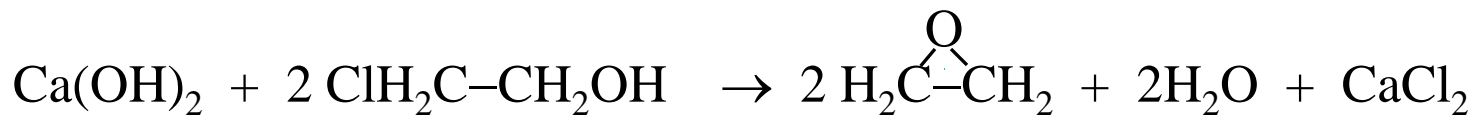
Illustrates the replacement of a classic organic reaction by a more economical catalyzed gas-phase flow process.

1. Chlorohydrin Process (no longer used on an industrial scale)

- the older method to make ethylene oxide generated ethyl chlorohydrin by the addition of Cl_2 and water



- treatment of the chlorohydrin with $\text{Ca}(\text{OH})_2$ gave the product



- high yields (85 %), but there are problems with the chlorohydrin process:
 - ◆ the use of expensive Cl_2
 - ◆ disposal of the CaCl_2 byproduct

Chemicals Derived from Ethylene

Oxidation of Ethylene to Ethylene Oxide

2. Direct Oxidation Using Air

The challenge here is to do a **controlled partial “burn” of ethylene** stopping at only 10 % of the energy release for the complete oxidation of ethylene to carbon dioxide and water:



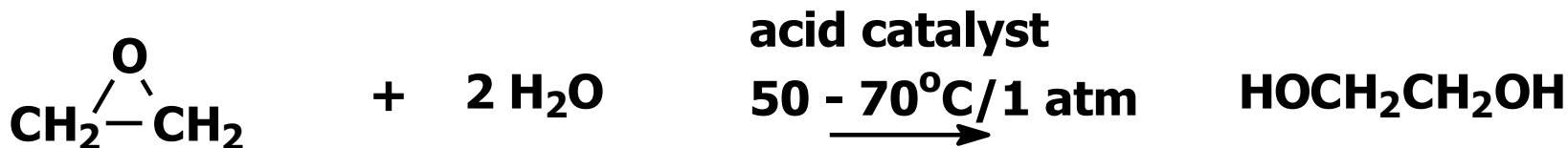
- silver is used to activate O₂ for the mild oxidation of ethylene to ethylene oxide
- essential to carry off the heat produced to prevent runaway oxidation
- this is done with a cooling bath of boiling kerosene
- the hot kerosene is used to generate superheated steam
- some ethylene is lost by oxidation “too far” to CO and H₂O
- lower ethylene oxide yield (75 %) than the chlorohydrin process yield (85 %)
- but the direct air oxidation process is more economical overall (no Cl₂ required)

80 % of the total ethylene oxide produced is used to make ethylene glycol, ethanolamines and ethoxylate surfactants

Chemicals Derived from Ethylene

Ethylene Glycol from the Hydration of Ethylene Oxide

- ethylene oxide is very reactive
- gentle treatment with aqueous acid gives ethylene glycol



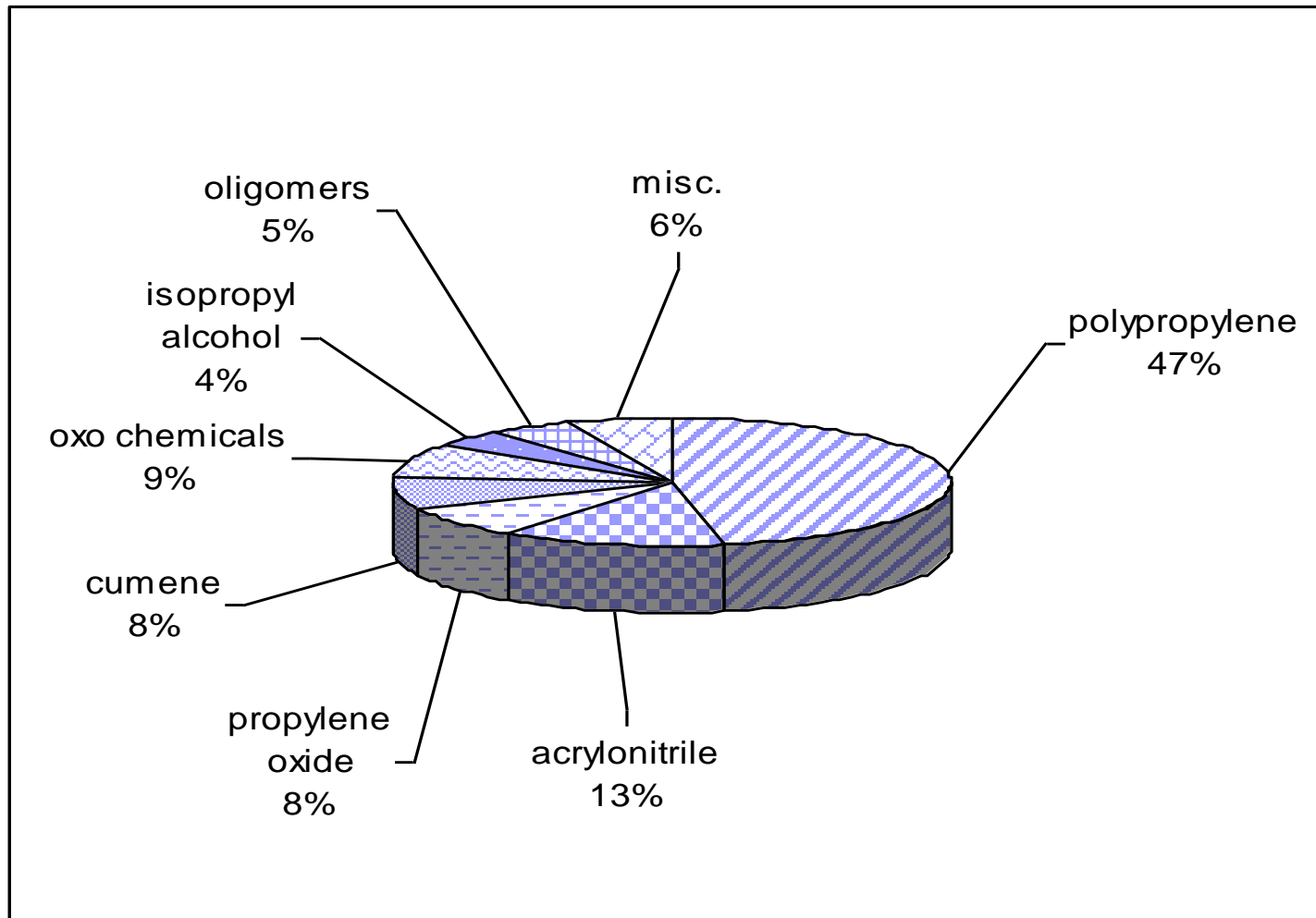
- a 5-fold molar excess of H₂O is used to limit the formation of diethylene glycol, triethylene glycol, and higher oligomers
- ethylene glycol is purified by vacuum distillation
- 10 % of total ethylene production is used to make ethylene glycol
- 80 % of the ethylene glycol production is used for antifreezes and for the synthesis of polyesters for fibers and plastic bottles

3.4 Chemicals Derived from Propylene (C3 Chemistry)

Propylene

- propylene, like ethylene, is formed by the steam cracking of hydrocarbons
- 50 to 70% of the propylene is used by the petroleum refining industry for the alkylation and polymerization to oligomers which are added to gasoline
- a smaller amount of propylene is purified for chemical manufacture
- the largest non-petroleum refining use of propylene is for the production of polypropylene
- acrylonitrile from propylene is polymerized to plastics and fibers
- propylene oxide is used in polyurethane plastic and foam
- cumene is made from propylene and benzene and is in turn converted to acetone and phenol
- isopropyl alcohol is also made from propylene

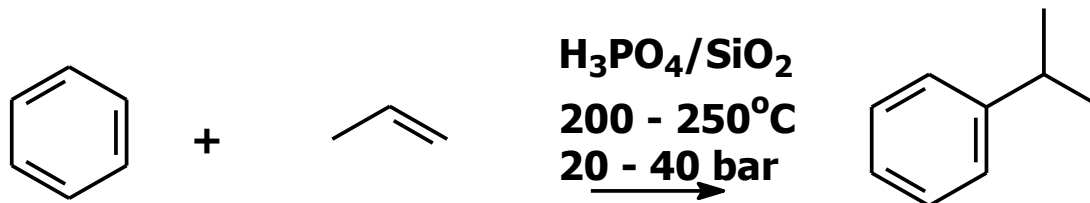
Chemicals Derived from Propylene



Chemicals Derived from Propylene

Propylene to Cumene (Isopropylbenzene)

- uses the Friedel-Crafts alkylation of benzene with propylene (analogous to the alkylation of benzene with ethylene to make ethyl benzene)



- important for the conversion to phenol and acetone

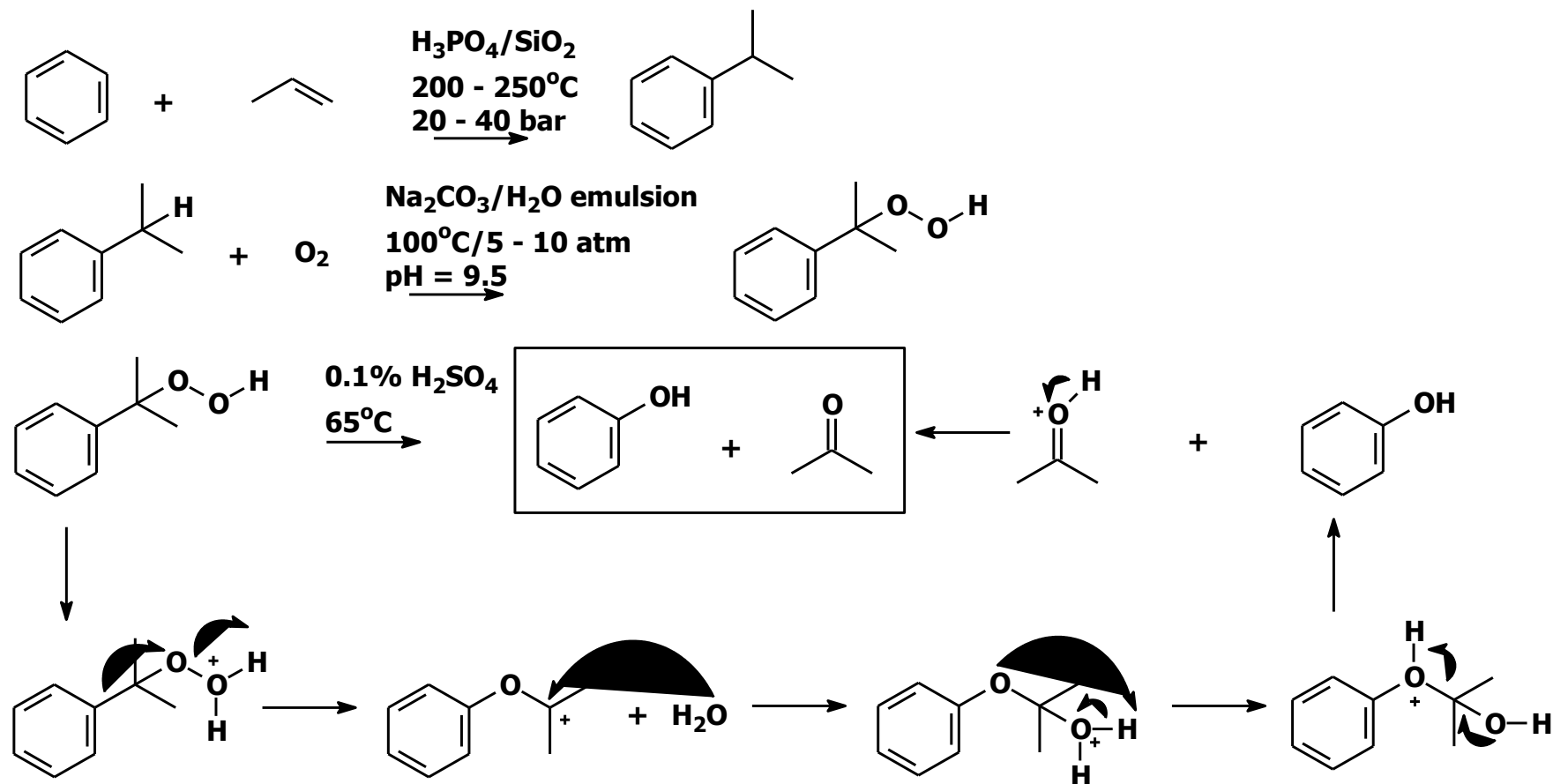
Acetone

Prepared commercially in three ways:

- a **Wacker-type partial oxidation** of propylene
- dehydrogenation (oxidation) of isopropanol
- coproduction in the **Hock phenol process** (most important)

Chemicals Derived from Propylene

Hock Process for Making Phenol and Acetone from Propylene



Chemicals Derived from Propylene

Phenol is used for:

- phenol-formaldehyde resin (BakeliteTM) (46 %)
- ϵ -caprolactam production via cyclohexanone (14 %)
- bisphenol A (14 %)
- adipic acid (3 %)
- other chemical intermediates (23 %)

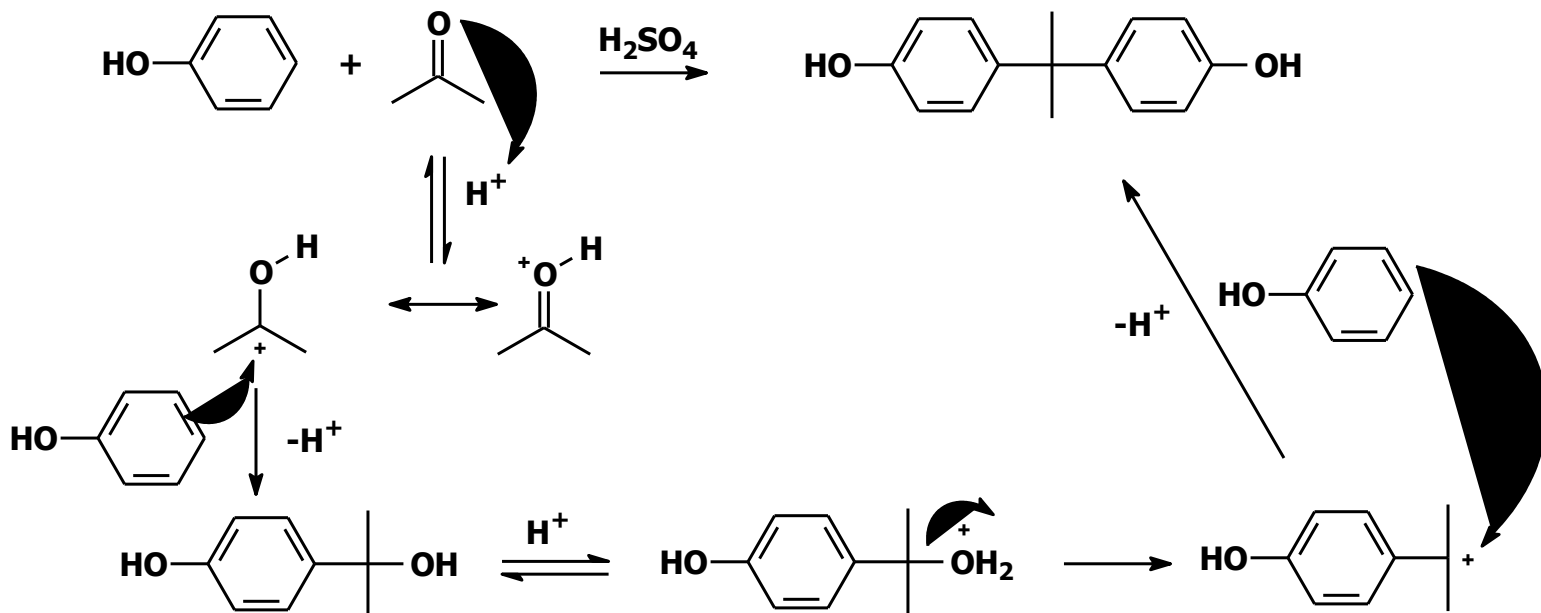
Acetone is used for:

- a solvent (20 to 30 %)
- methyl isobutyl ketone (MIBK) and methyl isobutyl carbinol (MIBC) (25 %)
- methyl methacrylate (18 %)
- bisphenol A, ketene, diacetone alcohol, mesityl oxide, *etc.*

Chemicals Derived from Propylene

Bisphenol A

- phenol is very reactive towards electrophilic substitution
- phenol reacts readily with acetone in the presence of an acid catalyst
- acetone is bulky enough to only react in the para position
- this leads, conveniently, to the single product bisphenol A (BPA)
- after the first substitution, a carbocation from the intermediate product is easily generated which then can substitute a second phenol
- BPA is a starting material for polycarbonate and epoxy polymers
- also used to line food and beverage cans



Chemicals Derived from Propylene

Propylene Oxide

Two processes are used to make propylene oxide:

- ◆ a chlorohydrin process
- ◆ indirect oxidation

Interestingly, the direct oxidation process used to make ethylene oxide from ethylene is not feasible for propylene due to the competitive reactivity of the allylic position.

Chlorohydrin Process for Making Propylene Oxide

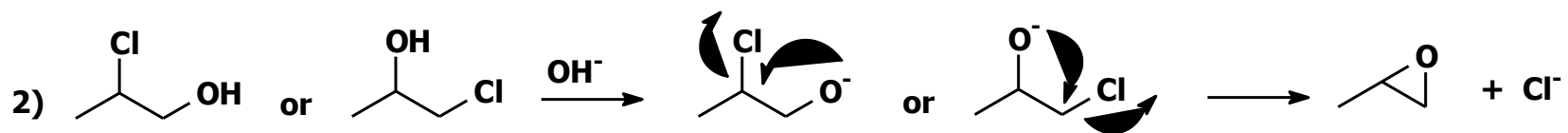
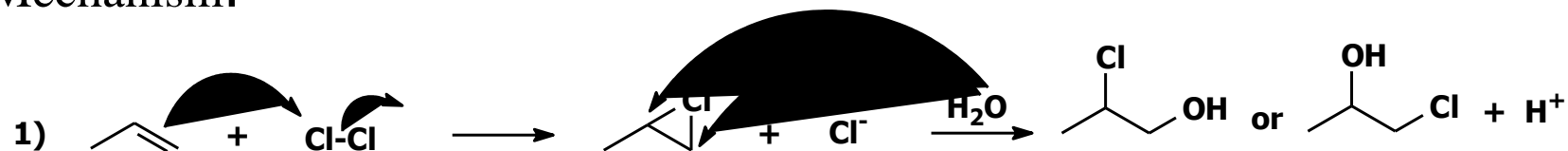
Two steps at 35 to 50 °C and 2 to 3 atm:

1. addition of HOCl (formed by hydrolysis of aqueous Cl_2) to the double bond
 2. intramolecular displacement of Cl^- and subsequent loss of a proton ($-\text{HCl}$)
- a mixture of two regioisomeric chlorohydrins is formed, used without separation
 - the product is driven off with steam and purified by fractional distillation
 - expensive chlorine used in the process is converted to low-value CaCl_2
 - other processes are under investigation

Chemicals Derived from Propylene

Chlorohydrin Process for Making Propylene Oxide

Mechanism:



- the α -chlorohydrin and β -chlorohydrin are formed in a 9:1 ratio
- steam is used to drive out propylene oxide which is purified by distillation
- 90 % yield
- main impurity is 1,2-dichloropropane

Chemicals Derived from Propylene

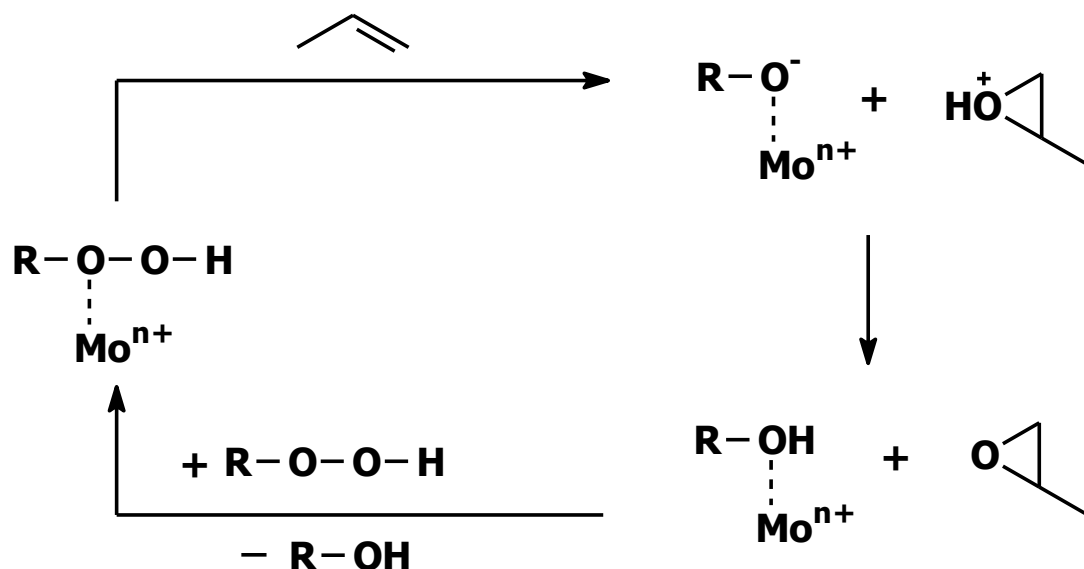
Indirect Oxidation Process for Making Propylene Oxide

Based on the observations that hydroperoxides and peroxy-carboxylic acids in liquid phases can selectively transfer their peroxide oxygen to olefins to form epoxides.

The hydroperoxides or peroxy-carboxylic acids are formed by the air oxidation of acetaldehyde, cyclohexane or isobutane, ethylbenzene or cumene.

Liquid isobutane or ethylbenzene are used as solvents.

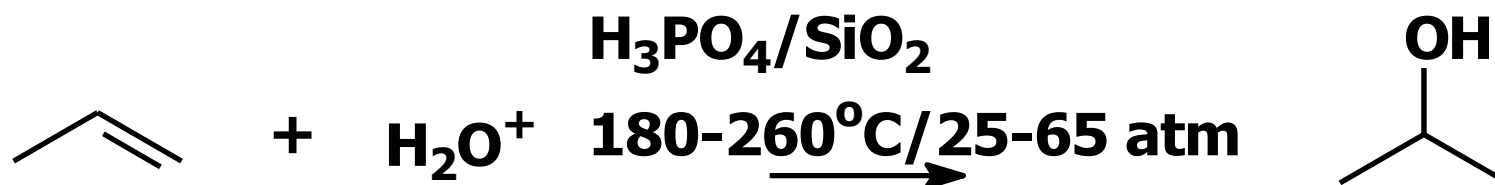
Mechanism



Chemicals Derived from Propylene

2-Propanol by the Hydration of Propylene

- analogous to the hydration of ethylene to make ethanol
- but the secondary propyl carbenium is more stable than the primary ethyl carbenium, so higher conversions are obtained with propylene than with ethylene
- very little *n*-propanol is produced (Markovnikov's rule is obeyed)



- exothermic ($\Delta H^\circ = -50 \text{ kJ mol}^{-1}$) and converts two molecules to one
- therefore favored by high pressures and low temperatures
- but the catalysts are only effective temperatures $> 180 \text{ }^\circ\text{C}$, so it is not possible to benefit from the thermodynamic advantage of low temperatures

Chemicals Derived from Propylene

Acetone

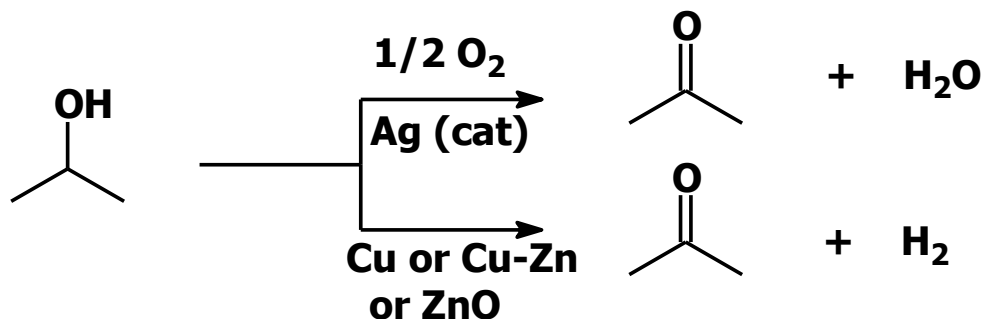
The most important method for the industrial production of acetone is the **Hock process** for the oxidation of cumene, already discussed. Smaller amounts of acetone are prepared by:

Oxidation of Propylene



Oxidation or Dehydrogenation Isopropanol from Propylene

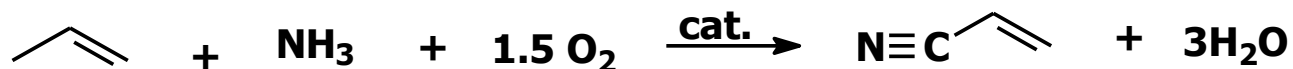
- these are catalytic processes at 500 °C and 40 to 50 psi
- the product is purified by distillation
- conversion of 70 to 85 % per pass and a yield of 90 %



Chemicals Derived from Propylene

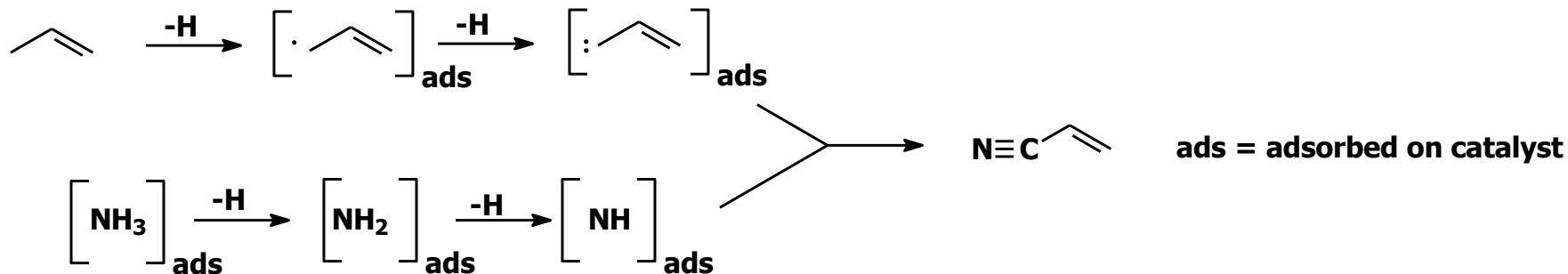
Acrylonitrile by Ammoxidation of Propylene

- acrylonitrile is copolymerized with butadiene to make synthetic rubber
- other applications include fibers, resins and thermoplastics
- acrylonitrile is second only to poly(propylene) a chemical use for propylene
- **ammoxidation** of propylene is the main source of acrylonitrile:



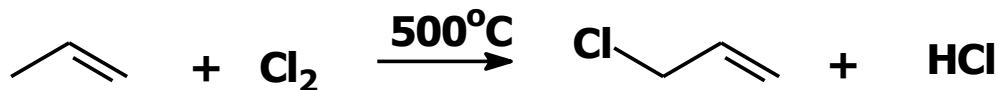
- ammoxidation denotes the catalytic oxidative reaction of activated methyl groups with ammonia to form nitrile groups

The course of the reaction proceeds as follows:



Chemicals Derived from Propylene

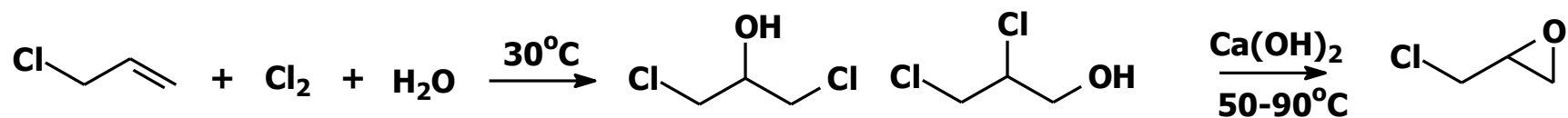
Allyl chloride



- the difficulty with this process is to get a radical reaction and to suppress the electrophilic addition of the chlorine
- this is accomplished by using high temperatures and excess propylene.
- even so, there are byproducts formed (1,3-dichloropropene, 2-chloropropene, 1,2-dichloropropane)

Epichlorohydrin

- made by an old-fashioned route

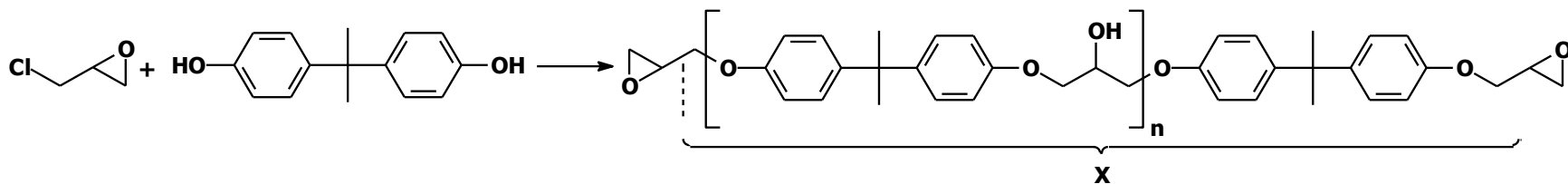


- used in epoxy resins
- can be hydrolyzed to glycerol but not cost effective *versus* isolation from natural sources

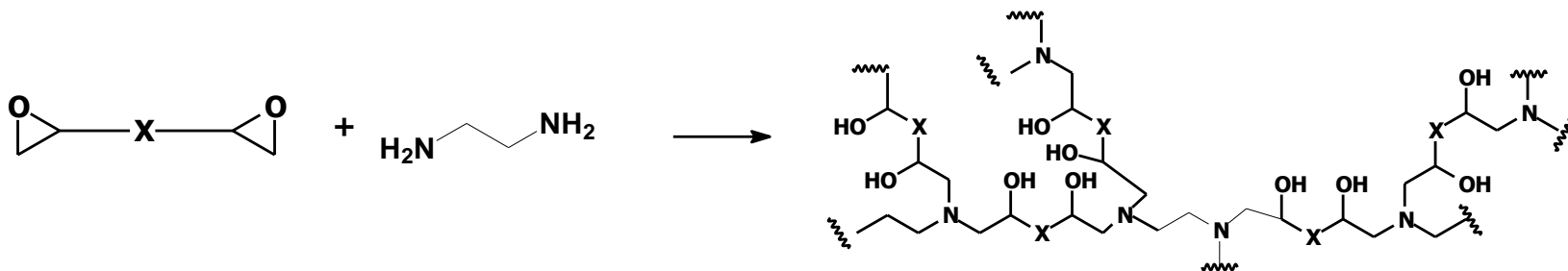
Chemicals Derived from Propylene

Epoxy Resins

A low molecular weight epoxy compound is formed by reacting epichlorohydrin and bisphenol A:



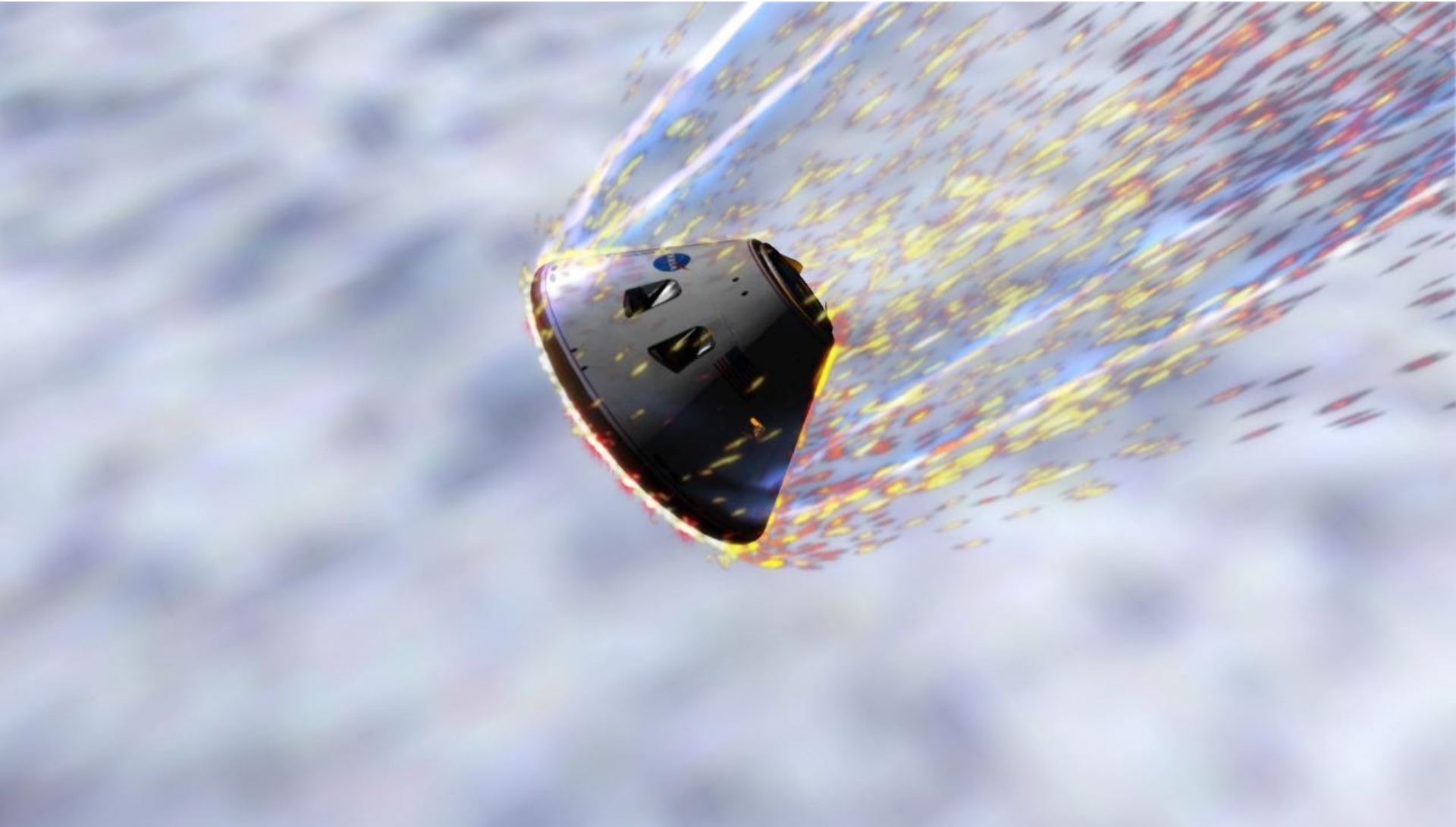
- cross-linking of these low molecular weight epoxy compounds is promoted by adding a curing agent such as ethylenediamine
- the primary amines react with the epoxides to form tertiary amines and branches
- a very tough three-dimensionally cross-linked polymeric structure results:



Chemicals Derived from Propylene

Epoxy Resins – *tough!*

Epoxy Resin Ablative Heat Shield on Apollo Crew Capsule



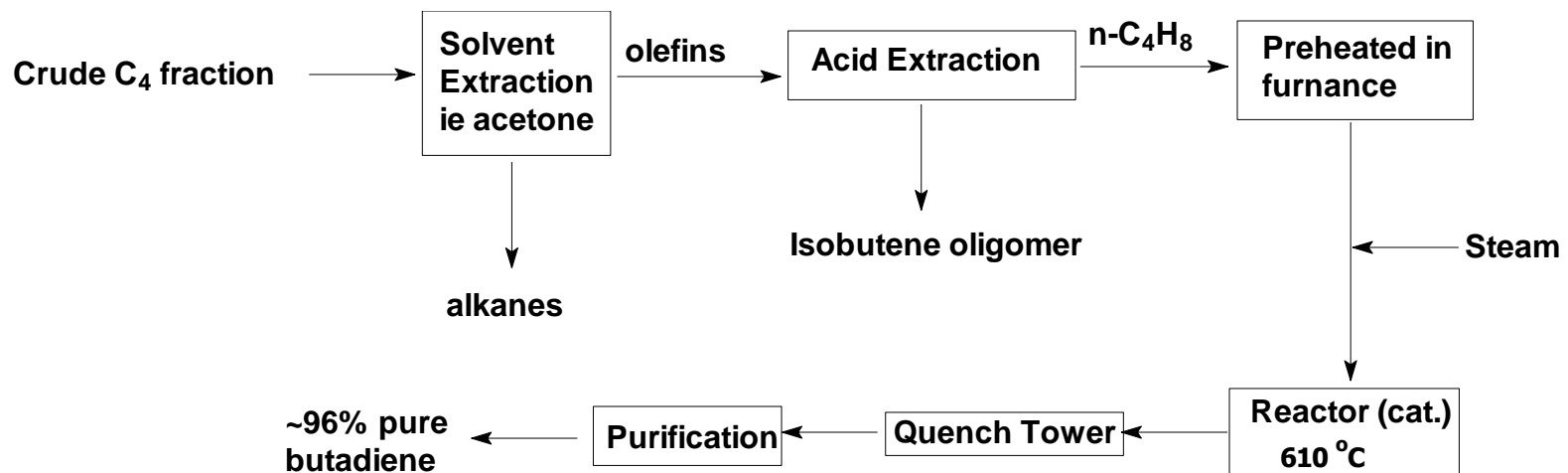
3.5 Chemicals From the Butylenes (C₄ Fraction)

1,3-Butadiene

- most important industrial diene
- used as a monomer and co-monomer for polymers such as styrene-butadiene rubber (SBR) rubber, butadiene rubber (BR)
- there has been a restriction in the availability of butadiene due to a decrease in C₄ dehydrogenation due to high costs and the use of lighter cracking feedstocks

There are two modern routes by which most butadiene is produced:

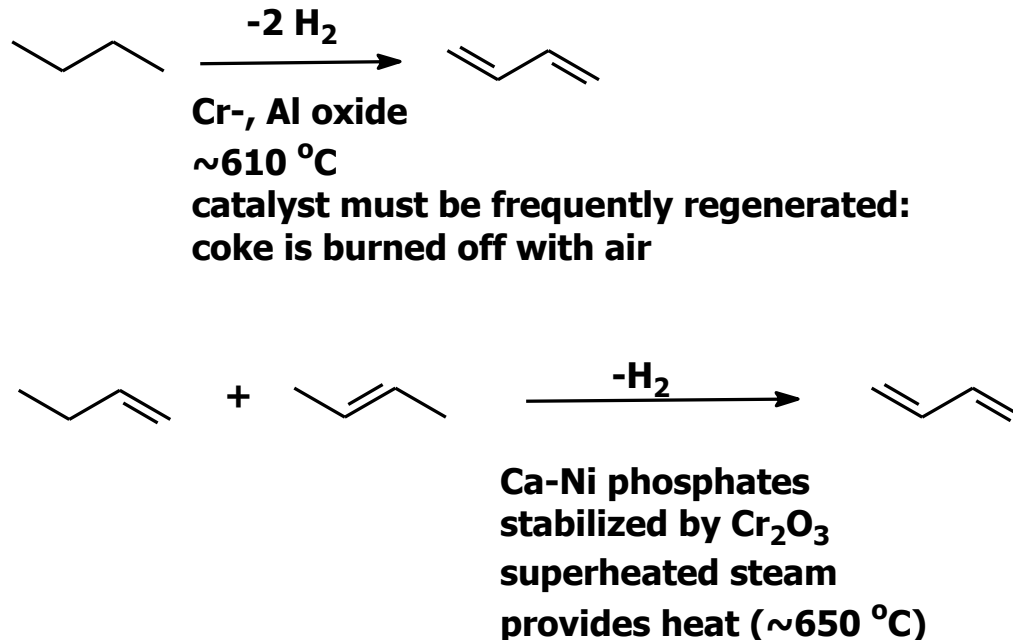
1) Isolation from the C₄ fraction obtained by thermal cracking of naphtha



Chemicals From the C4 Fraction

1,3-Butadiene

2) Dehydrogenation of *n*-butenes and *n*-butane

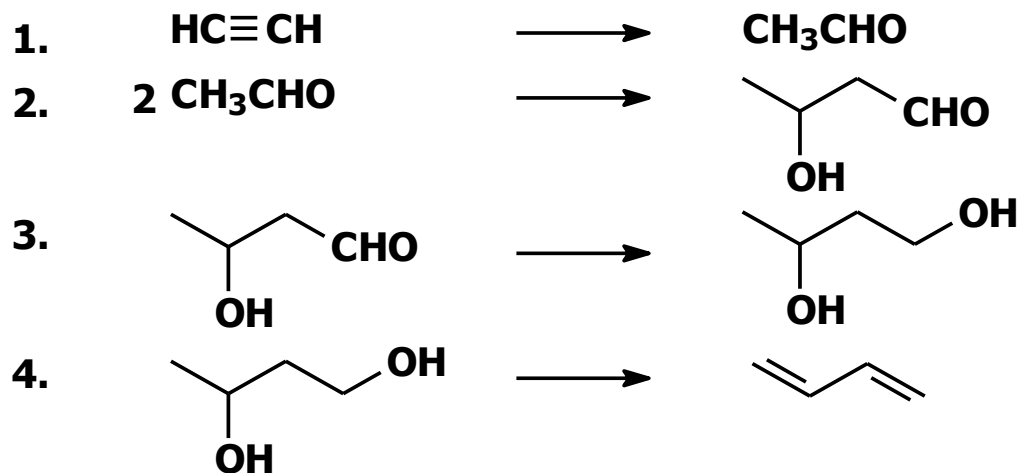


Chemicals From the C4 Fraction

1,3-Butadiene

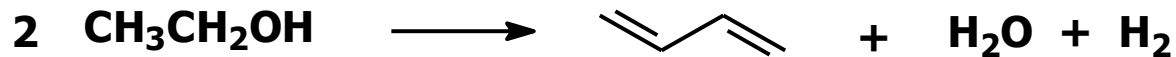
Two less important two synthetic routes for 1,3-butadiene production:

from acetylene



from the Lebedew process (in one step from ethanol)

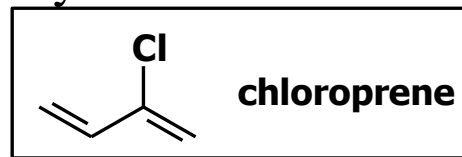
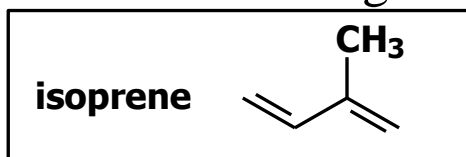
Could be used in countries with little petroleum and ample ethanol from fermentation



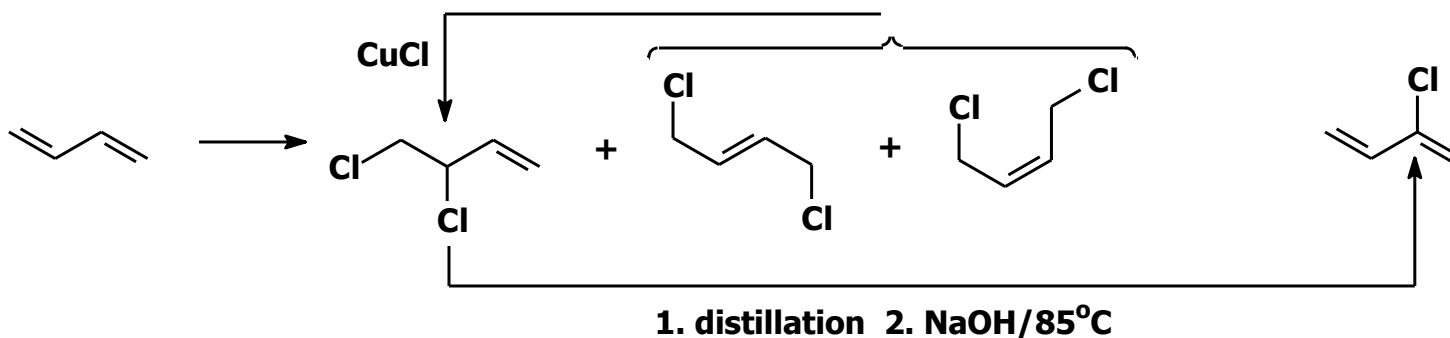
Chemicals From the C4 Fraction

Chloroprene

- chloroprene is named by analogy to isoprene
- CH₃ and Cl are of similar size as a substituent so it was felt that the resulting polymers would have similar properties
- the polymer derived from chloroprene is called neoprene, a synthetic elastomer
- neoprene is resistant to sunlight and oil, very useful features



- chloroprene is prepared by the radical chlorination and subsequent dehydrochlorination of butadiene
- Only the 3,4-dichlorobutene undergoes elimination to the desired product so it is distilled out of the mixture of dichlorobutenes
- CuCl is used to equilibrate the mixture to isomerize the undesired isomers to more of the 3,4-dichlorobutene
- elimination occurs with sodium hydroxide



Chemicals From the C4 Fraction

Polymerization of Butadiene and Chloroprene

- butadiene is polymerized using a variety of catalysts:

1,4-polymers

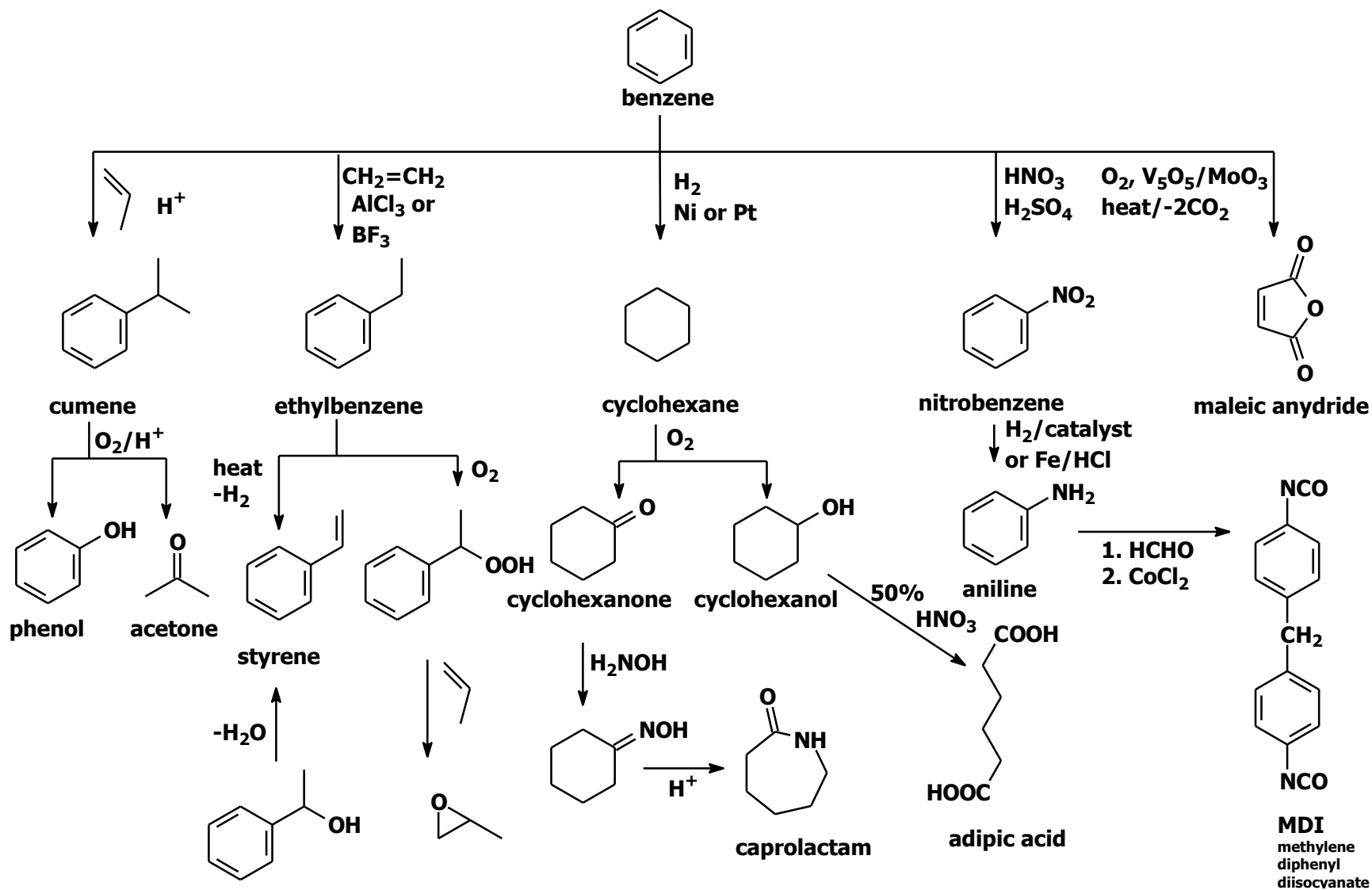


1,2-polymers



- chloroprene is polymerized using $K_2S_2O_8$
- the same conditions are used to prepare a copolymer of styrene and butadiene (this is the primary synthetic rubber)
- other reactions will be discussed in the polymer chemistry section

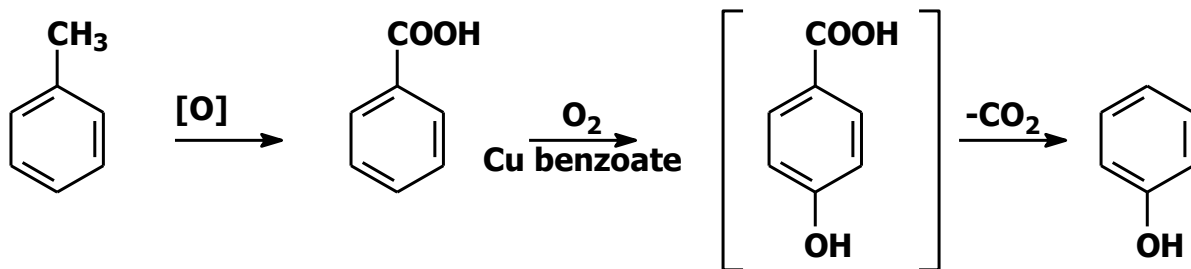
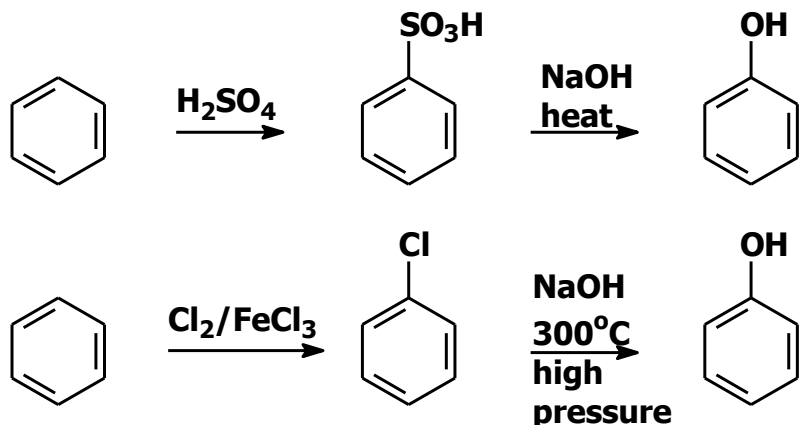
3.6 Benzene, Toluene and Xylenes (BTX)



BTX and Relatives (Benzene)

Phenol

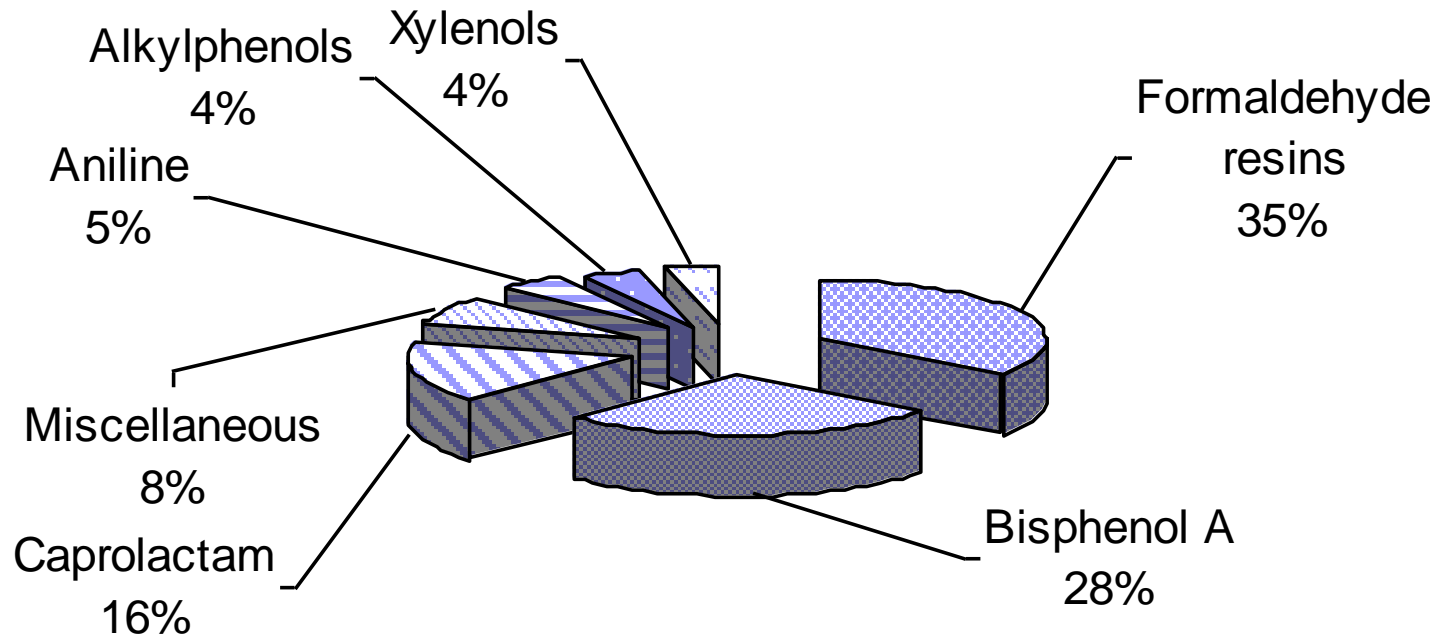
- major route to phenol is the cumene hydroperoxide rearrangement discussed earlier which accounts for 97 % phenol production
- other routes to toluene use electrophilic aromatic substitution:



- small amounts of phenol are obtained by the distillation of petroleum

BTX and Relatives (Benzene)

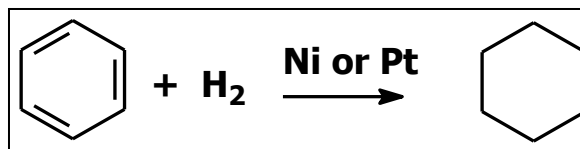
Uses of Phenol



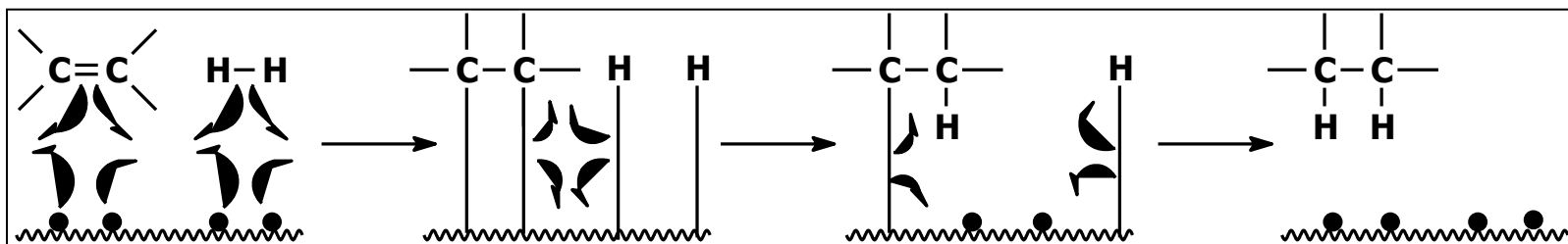
BTX and Relatives (Benzene)

Cyclohexane

- formed by the hydrogenation of benzene over a nickel or a platinum catalyst:



- although many catalytic reactions are not well understood, a large amount of work has gone into determining the hydrogenation mechanism which is thought to proceed as follows:



- the metal surface acts as a source of electrons
- the pi-bonds as well as molecular hydrogen bond to this surface
- the net effect is for the metal to assist in weakening the bonds to avoid a high energy free radical mechanism

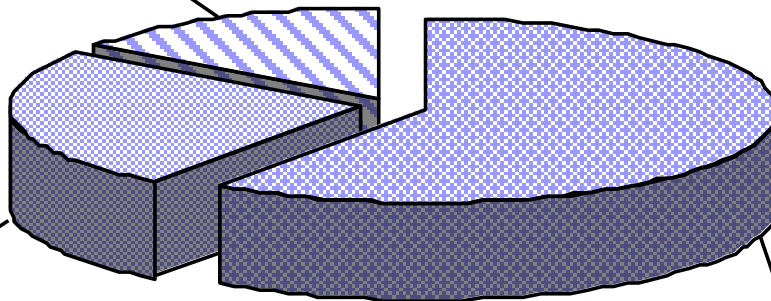
BTX and Relatives (Benzene)

Uses of Cyclohexane

Miscellaneous
15%

Caprolactam
25%

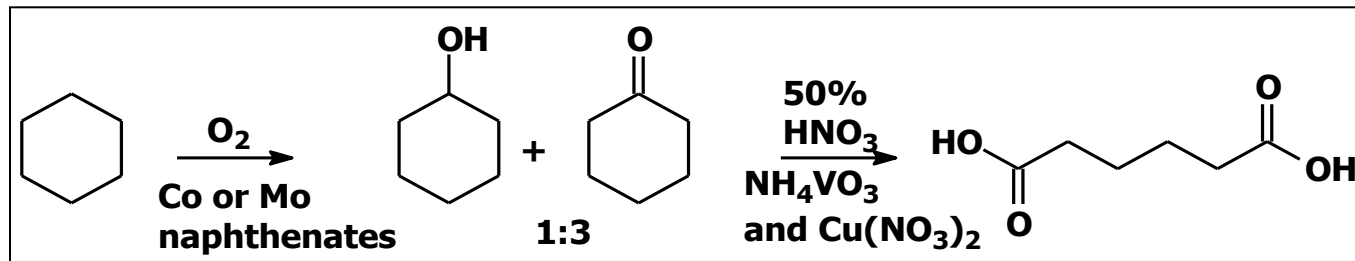
Adipic acid
60%



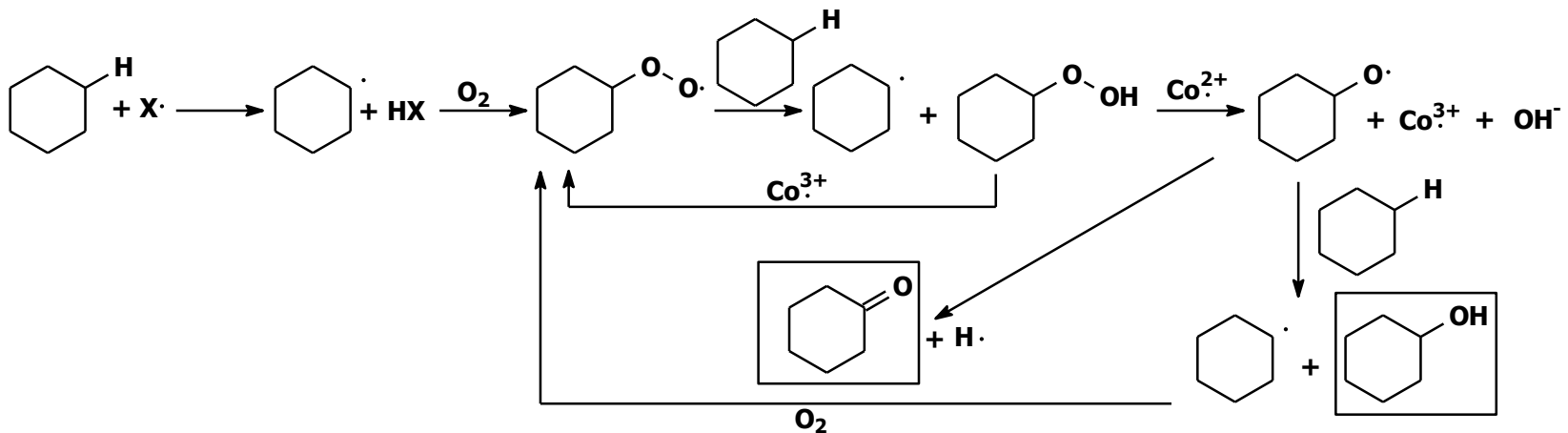
BTX and Relatives (Benzene)

Cyclohexanone and cyclohexanol to adipic acid

- most of the cyclohexane is converted to cyclohexanone and cyclohexanol
- yield 75 to 80 % yield
- the mixture ketone and alcohol obtained is then oxidized further to give adipic acid in about 95% yield

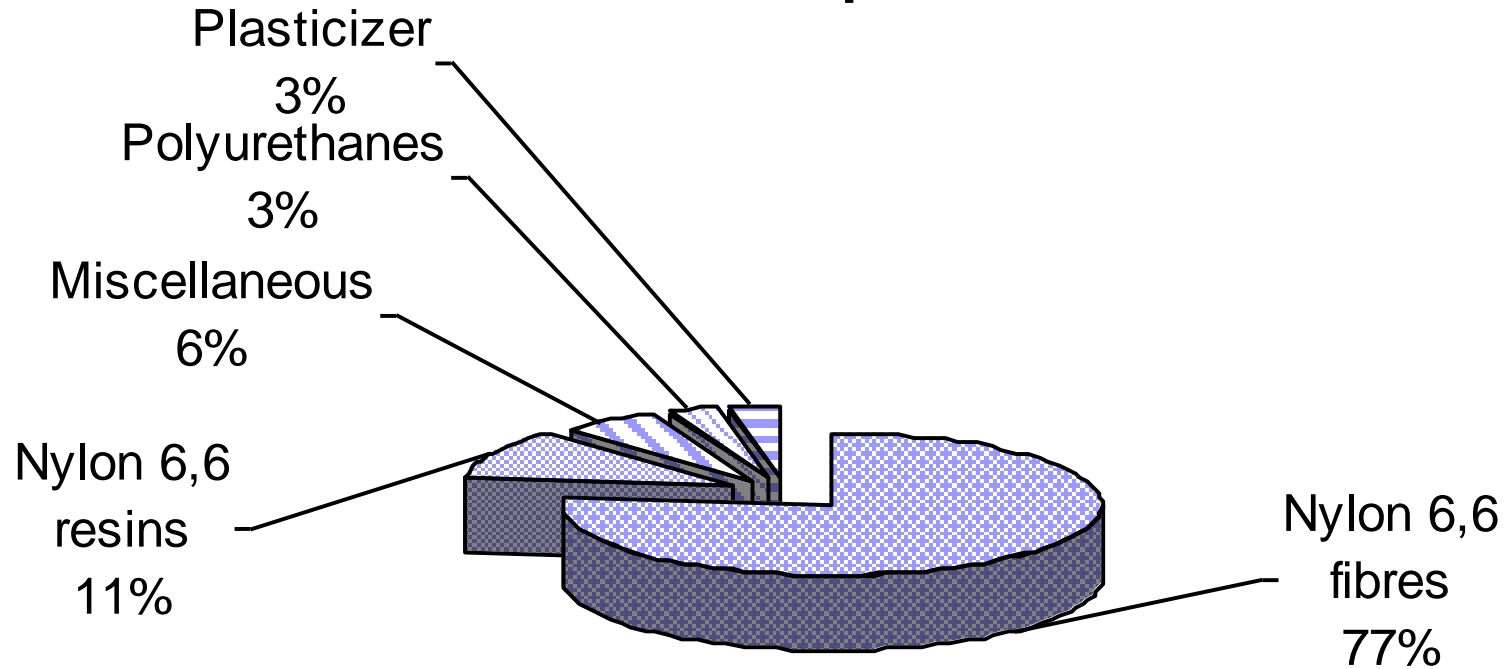


- naphthenates are salts of cyclic aliphatic hydrocarbon acids
- the oxidation to cyclohexanone and cyclohexanol is proceeds as follows:



BTX and Relatives (Benzene)

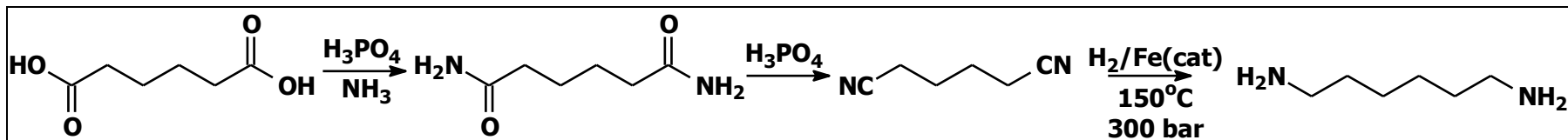
Uses of Adipic Acid



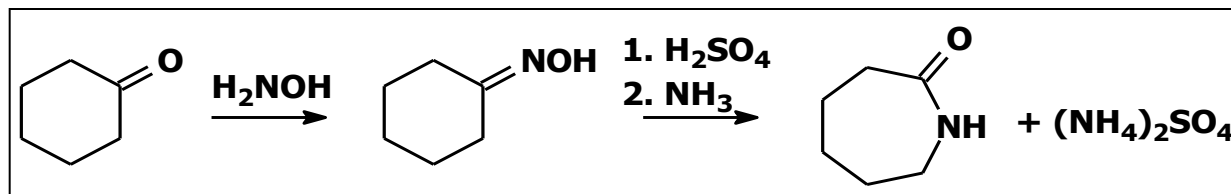
BTX and Relatives (Benzene)

Adipic acid to adiponitrile and hexamethylene diamine

- adipic acid is converted to adiponitrile by way of the amide
- H_3PO_4 is the catalyst (strong but not too strong to tie up the ammonia)
- the acid assists in the dehydration to the nitrile
- adiponitrile can be hydrogenated to hexamethylene diamine



- adipic acid and hexamethylenediamine are polymerized to make **nylon 66**
- the caprolactam monomer for nylon is made from cyclohexanone by the oxime:

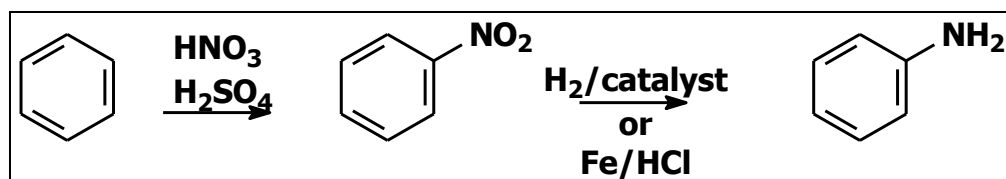


- the formation of the oxime and the subsequent Beckmann rearrangement are well known mechanisms
- caprolactam is polymerized by heating in the presence of catalytic water at 250 °C for 12 hours at 20 bar

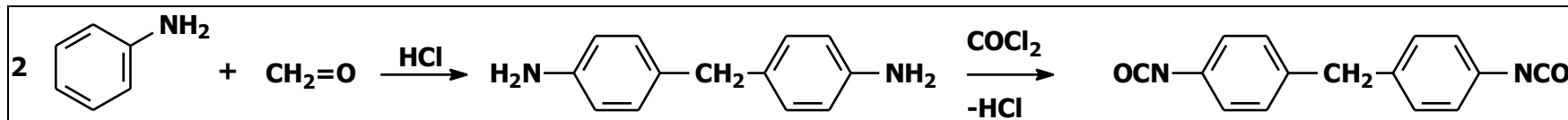
BTX and Relatives (Benzene)

Nitrobenzene and Aniline

- aniline is prepared in two steps from benzene by nitration followed by reduction

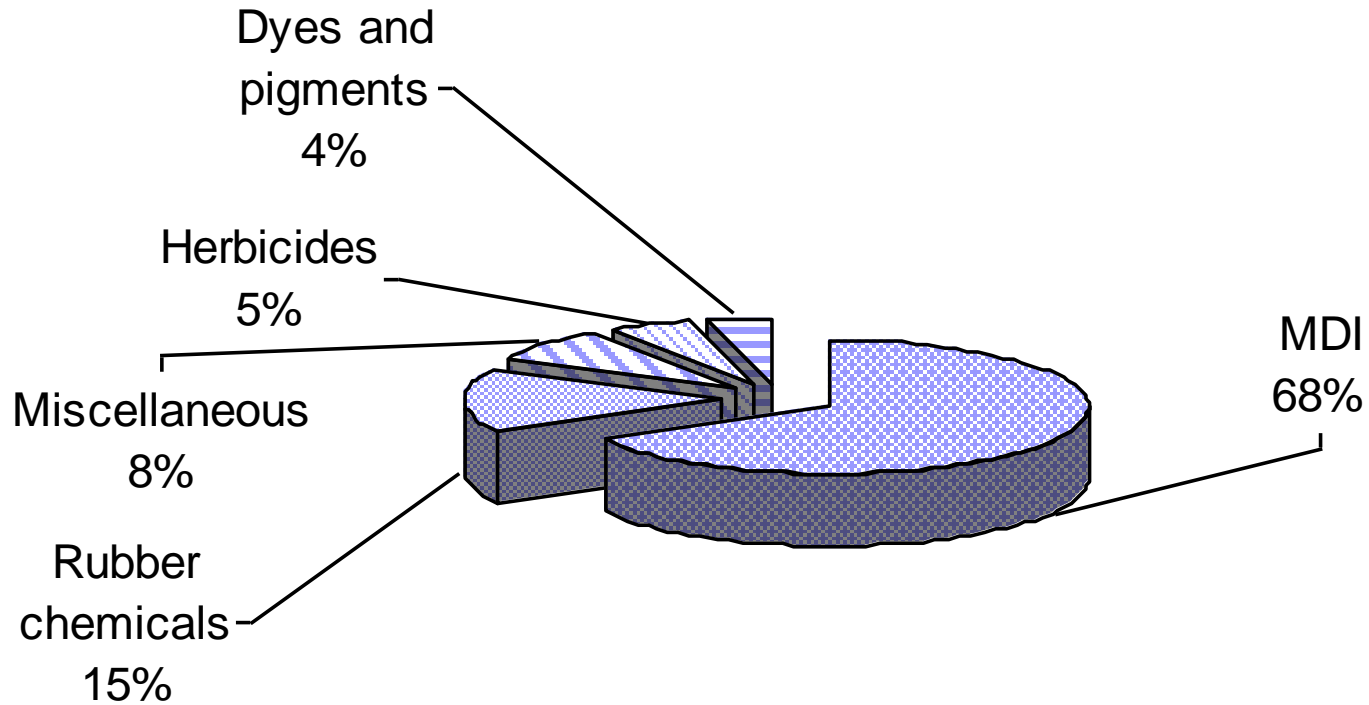


- hydrogenation has replaced the iron-mediated reduction
- aniline is used in the rubber industry in the manufacture of vulcanization accelerators and as age resistors
- most aniline is used to make methylene diphenyl diisocyanate which is polymerized with a diol to form a polyurethane

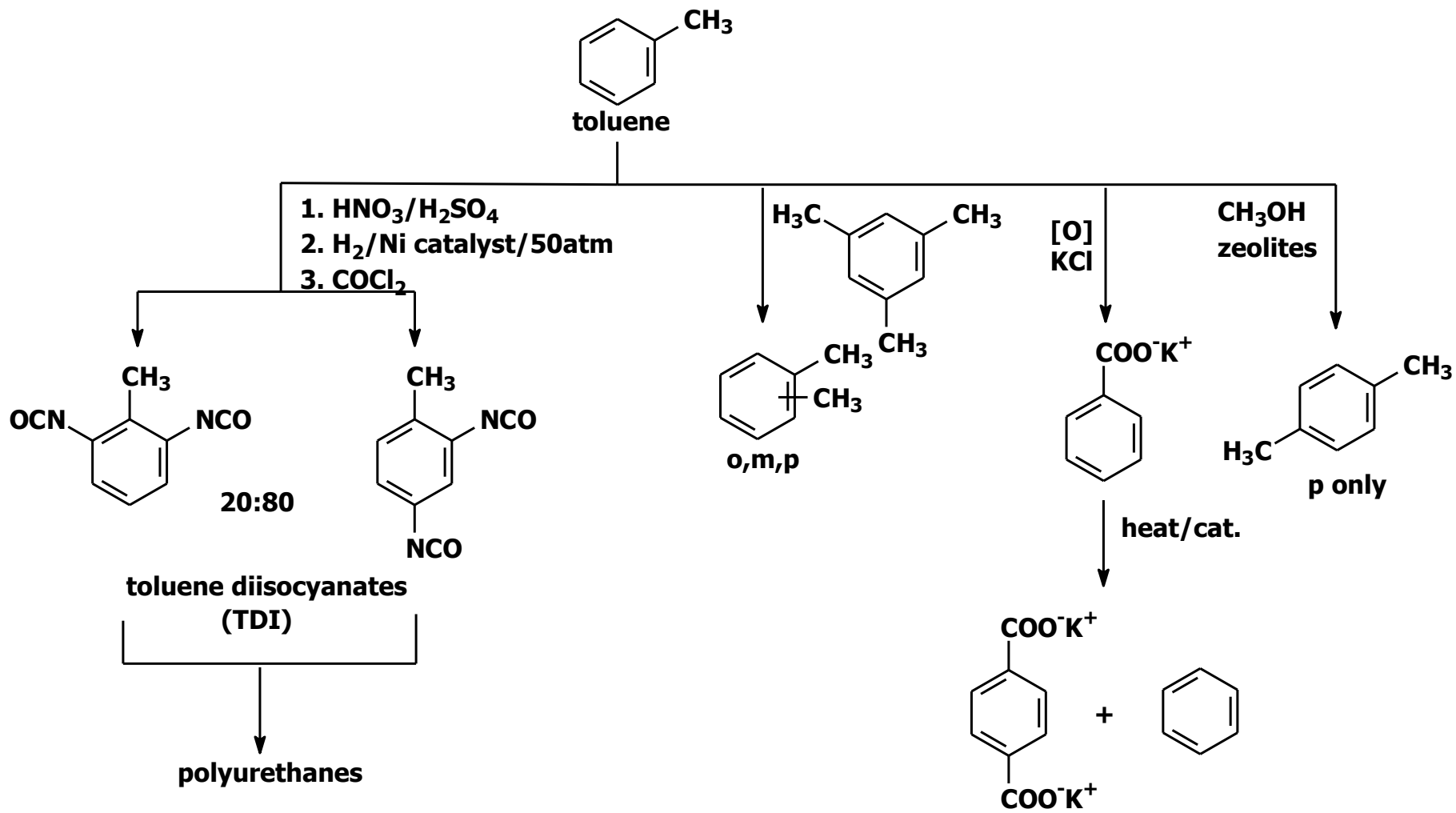


BTX and Relatives (Benzene)

Uses of Aniline



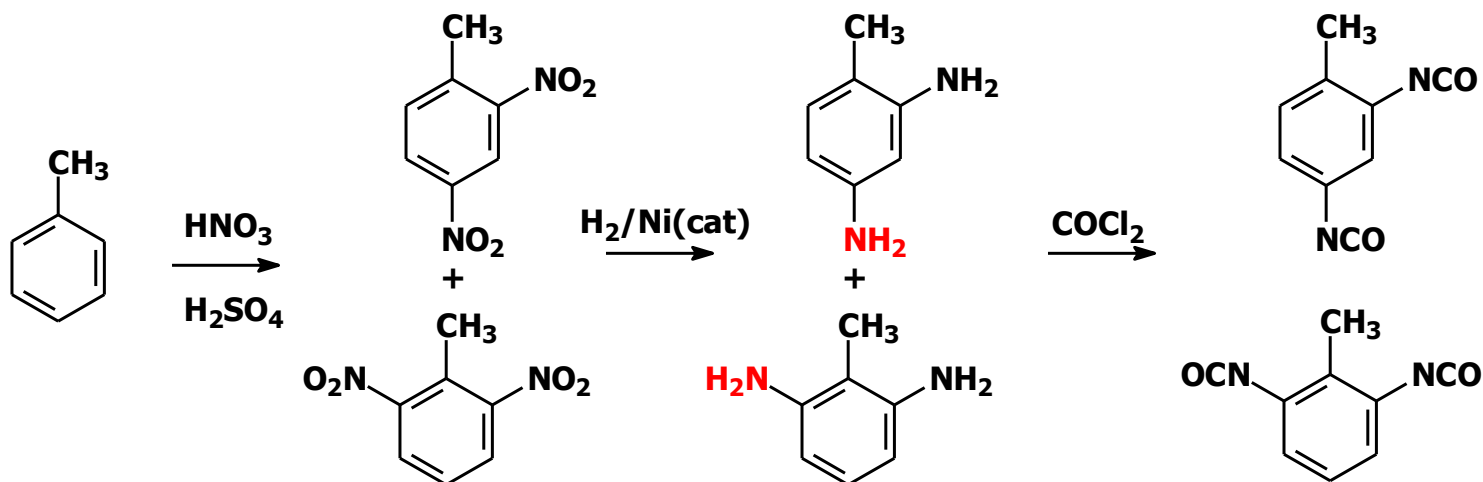
BTX and Relatives (Toluene)



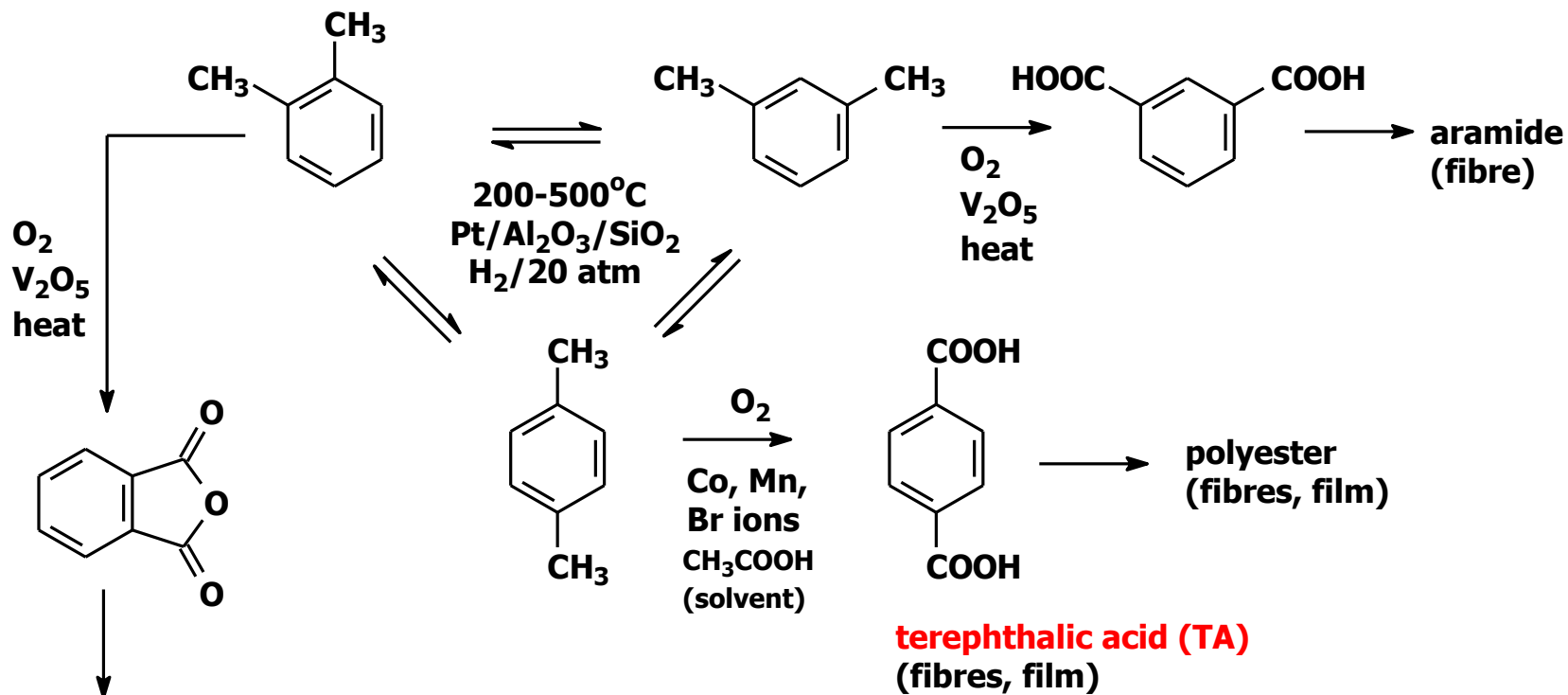
BTX and Relatives (Toluene)

Toluene-2,4-diisocyanate and -2,6-diisocyanate

- toluene is nitrated to a 80:20 mixture of 2,4 and 2,6 dinitrotoluene
- the nitro groups are then reduced to the amino groups
- H_2 on a Ni catalyst is used instead of a more expensive metal reducing agent
- liquid-phase reaction is used to reduce the explosion hazard of the dinitrotoluene
- treatment with phosgene converts the diamine to the diisocyanate
- the phosgene is made by the reaction of CO with Cl_2
- a problem with this reaction is that HCl ties up the unreacted amine preventing it from becoming the isocyanate



BTX and Relatives (Xylenes)



phthalic anhydride

resins: alkyd (paints), polyester (laminated plastics)

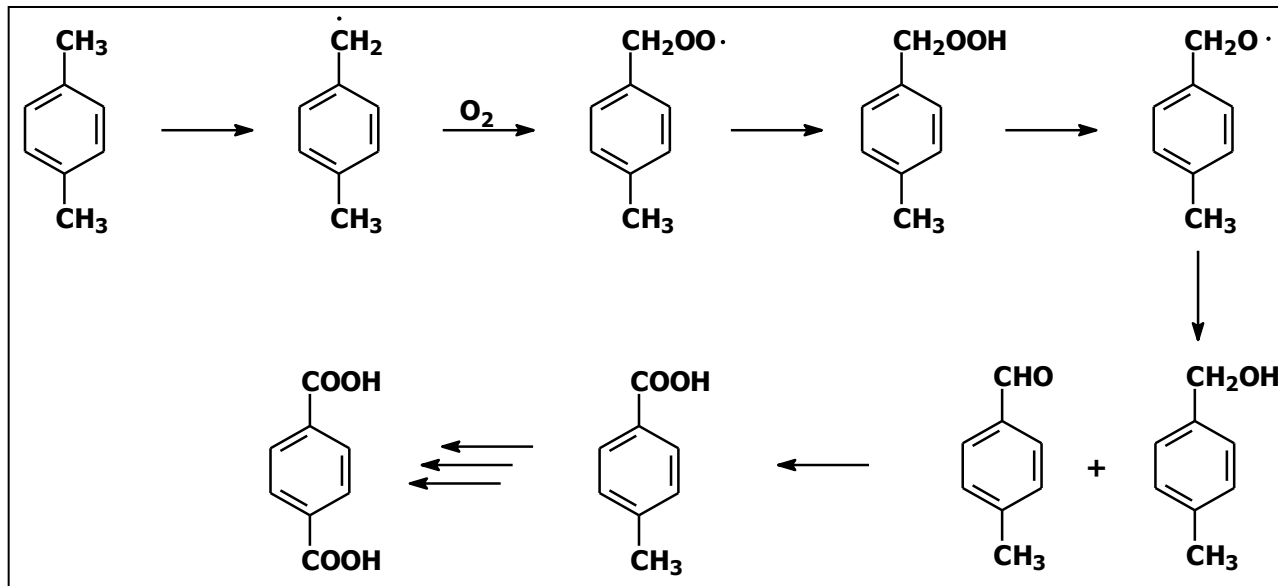
plasticizers

terephthalic acid (TA)
(fibres, film)

BTX and Relatives (Xylenes)

Terephthalic acid and dimethyl terephthalate

- oxidation of *p*-xylene is performed in the presence of Co and Mn salts of bromides at 200 °C and 30 bar
- a simplified mechanism (similar to other oxidations discussed previously):



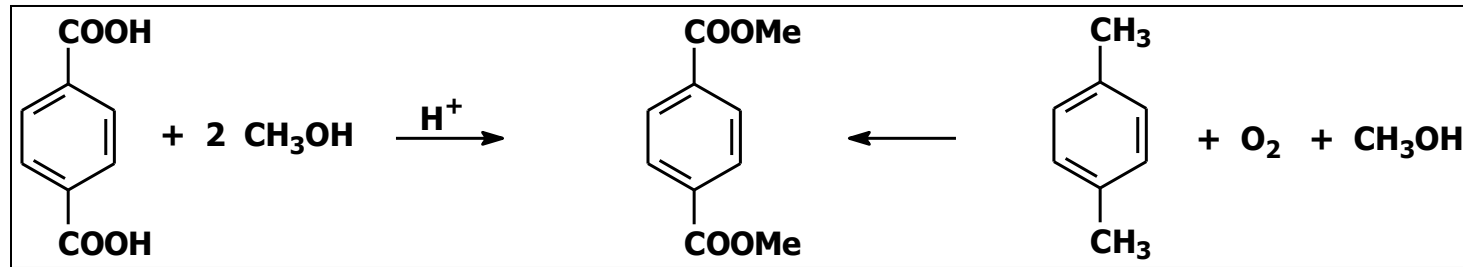
- the crude terephthalic acid (TA) is cooled and crystallized
- the xylene and acetic acid are evaporated
- TA is washed with hot water to remove acetic acid and catalyst
- some *p*-formyl benzoic acid present (a problem for subsequent polymerization processes) is removed by reduction to *p*-methyl benzoic acid followed by a recrystallization to yield 99.9 % pure TA

BTX and Relatives (Xylenes)

Terephthalic acid and dimethyl terephthalate

Dimethyl terephthalate (DMT) is made from crude TA or from *p*-xylene by

- esterification of TA with methanol using sulfuric acid catalysis
- direct oxidation of *p*-xylene with methanol using copper/manganese salt catalysis



- crude DMT must be carefully purified using a five-column distillation system
- TA or DMT are reacted with ethylene glycol to form poly(ethylene terephthalate)
- can be reacted with other diols to make other polyesters
- poly(ethylene terephthalate) (PET) fibers are used for textiles and insulation
- PET films are used for packaging
- PET softened by heating is blown into molds to make disposable bottles